

Encyclopedia of Materials:
COMPOSITES

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ENCYCLOPEDIA OF MATERIALS: COMPOSITES

Volume 2

ENCYCLOPEDIA OF MATERIALS: COMPOSITES

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Volume 2

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Section 3: *Ceramics Matrix Composites*, Edited by Fatima Zivic

Section 4: *Smart Composite Materials*, Edited by Eva Pellicer

Section 5: *Processing of Composite Materials and Physical Characteristics*,
Edited by Dermot Brabazon



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PREFACE

This is the first *Encyclopedia of Materials: Composites* published by Elsevier which presents a vast and widely encompassing content in the area of composite materials science and engineering. Composite materials have become even more important and ubiquitous over the recent decades due to the many advantages that they can provide over single monolithic materials. This includes improvements in the properties such as the physical, electrical, chemical, optical and magnetic properties which can be achieved by combining two or more materials.

The two main types of composites, Metal and Polymer matrix based, are presented in detail within Sections 1 and 2 respectively while Ceramic matrix composites are presented in Section 3. Smart composites which is an area that is growing fast with increasing industrial relevance is covered in Section 4. Assessing the properties of composite materials thereby enabling their application is a crucial aspect of composite materials development and usage. As such, Section 5 presents the testing methods used and property results from the testing of composite materials. The design of composite materials is covered in Section 6. The recyclability and sustainability of materials used in products is an ever more important topic. There are some challenges to achieve well the recyclability of composite constructs. The Encyclopedia presented two Sections covering this one (Section 7) covering nature based composites and another covering the life cycle analysis of composite materials (Section 8). In the last section of the Encyclopedia, Section 9 covers how to join composite materials together and with more conventional monolithic materials.

As an Encyclopedia, these sections were prepared to be the primary central source of background knowledge for undergraduate, postgraduate and researchers studying or working with composites. The audience of this work covers both academic and industrial researchers. In today's composite materials market, engineers, architects, and even policy makers, need reference literature where to find definitions, concepts and state-of-the-art knowledge. As such this Encyclopedia will be an invaluable reference for engineers, architects, scientists, and policy makers.

Each section contains the articles written by world experts in their area. As well as providing the latest background information, the state of the art in the niche areas is presented in the individual articles. A particular concern in preparing these articles by the authors and Section editors was to make the content as accessible as possible to the reader. This is important given the multi-disciplinary nature of people working on the development and implementation of composite materials.

I take this opportunity to thank the 337 authors from across the world who have contributed the 171 articles to this Encyclopedia. It has been enjoyable to work with you are encouraging to see your expertise, interest and desire to help others from your contribution. With the many co-authored articles, there has been extensive collaboration which has resulted in a more informed and well-presented Encyclopedia content for the reader.

I am indebted also to the members of the Editorial team who have worked many long hours over the last couple of years to provide feedback and iterate on articles with the authors. The Editorial team have collectively many years of expertise working in their research areas. This team was formed via a variety networking events including conferences such as ESAFORM and Global Conference on Nanomaterial Forming (Manoj Gupta, Robertt Valente, Antonella Astarita), EU research projects and COST Actions (Fatima Zivic and Eva Maria Pellicer), and via other Dublin City University and sustainable engineering networking events (Mohamed El Mansori and Lorna Fitzsimons). I thank the Elsevier Major Reference Works team who supported in a professional manner the compiling of this work. In particular, I thank Laura Jackson, Sajana P K, and Ruth Rhodes for their direction and support throughout the preparation of this Encyclopedia.

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Ceramics Matrix Composites: An Introduction

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Ceramics matrix composites (CMCs) represent significant group of materials even though this type of composites is commonly considered as being less present in wider research and applications. In general, development of CMCs have been mainly focused on high technology industries like aerospace, or high energy systems (e.g., nuclear energy systems), where elements and systems operate under harsh conditions and high temperatures and pressures. On the other hand, these industries cannot openly share their research findings, due to strict confidentiality aspects in specific elements and systems that they utilize. Accordingly, published research results within a scientific literature are rather limited. Another aspect that rather prevents wider research on high-temperature ceramic composites is their cost of fabrication which is really high in comparison to polymer-based composites. Processing of CMCs usually requires special conditions involving high temperatures and pressures, meaning sophisticated setups and devices along with safety requirements in operation of these systems.

Very often, materials that belong to ceramic composites are not initially perceived as composites, such as concrete in construction industries, or wide group of novel biomedical composites based on ceramics. These CMCs do not have extremely high cost as in the case of aerospace and energy systems ceramics. Also, different new approaches in their fabrication have been studied and research publications in these fields are significantly more available. Especially biomedical devices represent significant development area. These composites are still more costly in comparison to traditional polymer or metal biomedical materials, but their properties justify those investments.

Ceramics Matrix Composites Volume within Encyclopedia of Materials: Composites, gathered the latest developments related to CMCs in different areas and applications. It starts with general overview of their properties, processing routes and application areas. Main reason for development of ceramic composites is the brittle nature of pure ceramics. Introduction of fibers, particles or whiskers in ceramic matrix has enabled control of crack and failure in material structure and general insights are presented. Overview of oxide and non-oxide ceramic matrices and different reinforcements are listed together with the latest research references, whereas alumina (Al_2O_3), zirconia (ZrO_2), and silicon carbide (SiC) accounts for the majority of applied matrices nowadays. Review of applications and the latest research directions are given, including high-temperature ceramics, bioceramics, carbon nanotubes (CNTs) and graphene, composites for energy conversion and storage, electromagnetic shielding, wear resistance and self-lubrication, as well as novel ultra-high temperature ceramic matrix composites (UHTCMCs).

Traditional and novel production technologies of ceramic composites are shortly presented, where solid phase processes (dry and wet sintering) represent around half of all processes. Sol-gel and reactive melt infiltration (RMI) are widely applied liquid phase processes, as well as Chemical Vapor Infiltration (CVI) within gas phase processes. Production technologies of different reinforcements (powders, particles, platelets and whiskers) are also shown. Sol-gel processing, filament winding and freeze gelation are discussed in more details and properties of such fiber-reinforced ceramic matrix composites. Sintering of ceramics as widely used thermal treatment is reviewed, as well as possibilities to control the microstructural properties.

Design of porous materials has introduced vast possibilities for controlling different material and functional properties of the components. Main properties, manufacturing, and applications of porous CMCs are presented, as well as influential factors related to controlled porosity and resulting mechanical properties. Properties of porous oxide CMCs and their applications and case studies in aerospace industries are shown.

New nanoparticles, especially based on carbon phases have become very important in composite design and development. Properties of the CMCs with carbon nanophases are presented, emphasizing tribological properties and electrical conductivity. Also, nanostructured multifunctional polymer-ceramic nanocomposites are described, with their applications in electronics and energy conversion, biomaterials and for environmental protection. Review of properties related to CMCs with metal particles as additives is also presented.

Characterization of composites is of the utmost importance for their appropriate functional applications and review of traditional and new techniques and methods in relation to ceramic composites are given: static mechanical characterization and non-destructive testing. Post processing and different influences on composites, either to improve some of the properties, or performance, both has significant effects on final material properties and functional life. Extremely harsh environments where CMCs are employed are within the advanced nuclear energy systems and radiation induced effects in CMCs are briefly presented. Also, laser processing introduces significant structural changes and some effects are described. Performance analysis of ceramic composites for bearing applications is given, with case studies. In material characterization, modeling of composite behavior is very important for optimized use of experimental resources, especially for high-cost materials as CMCs. Overview of important approaches in modeling of mechanical behavior of fiber reinforced composites and material modeling of concrete is given.

Final articles in this Volume present different applications and case studies of CMCs. Automotive industries use CMCs in components that operate under extreme temperatures, such as brake elements, turbine parts, valves and other, in order to provide high resistance and mechanical durability over time. Typical examples of ion conducting materials are presented focusing on superionic conductors and solid-state ionics. Application examples are described, such as sensors, lithium ion batteries, NaS

battery, solid oxide fuel cell (SOFC), electrolysis of gaseous molecules, gas separation and atomic switch or nano-ionics circuits. Possibilities of using carbon nanotubes in water and wastewater treatment systems are analysed.

Several articles are dedicated to the latest development in biomedical area. Application of composites in ophthalmology is presented, as well as biomaterials for bone tissue engineering. Drug delivery systems are analysed focusing on calcium phosphate (CaP) ceramics, CaP cements, bioactive glasses, and their architectural forms as coatings, particulates and scaffolds for drug delivery. Advanced dental ceramics are also presented including glass ceramic, lithium disilicate, leucite, veneering ceramic and zirconium based materials, especially important in esthetic dentistry.

General Overview and Applications of Ceramic Matrix Composites (CMCs)

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Introduction

Composites play a key role in numerous systems today. Composites with ceramic matrix provide specific properties related to strength, high temperature resistance, thermal stability and endurance, especially under high pressures, and high temperatures in a prolonged functional time. Ceramic matrix composites (CMCs) are used in versatile sectors from aerospace and transportation applications up to many other areas, like heat exchangers, gas turbines, high performance turbine engines, nuclear reactors, cutting tools, energy storage systems, medical devices, etc. They have exceptional properties of high hardness, heat resistance and resistance to corrosion. These composites can be used under temperatures ranging from very low to a very high, what is one of the specific characteristics of ceramics.

In general, ceramics have low density, high strength under very high temperatures, and they are not chemically reactive materials. Accordingly, ceramics are very good material for engineering applications that require operation under very high temperatures (turbine blades, automotive brakes, etc.), but also within chemically aggressive environments, such as human body (biocompatible ceramic-based implants and medical devices). However, pure ceramics extremely lack toughness and are prone to catastrophic failures, related to thermal or impact shocks, mainly caused by any existing flaws within the material structure. Processing of pure ceramics is complex and they can be easily damaged during production that can further induce internal or surface damage. Improvements of pure ceramics, by introduction of CMCs, have been aimed to overcome recognized issues, without compromising their excellent high temperature strength and environmental resistance (Chawla, 2019; Carter and Norton 2013; Warren *et al.*, 2000; Meetham and Van de Voorde, 2000). The main goal of CMC development initially was to prevent catastrophic failures. Incorporation of different reinforcements (fibers, particulates, platelets, whiskers) into the ceramic matrix results in toughened ceramic material. However, very high cost of CMCs has limited scope of research in ceramic-based materials, in comparison to other material classes (metal and polymer based materials) and large scope of research is focused on cost efficient fabrication methods.

Properties of Ceramic Matrix Composites (CMCs)

Design concept of ceramic matrix composites is different than those with metal or polymer matrix. Reinforcements in CMCs are not introduced to bear the load as in the case of metal or polymer matrix composites. Distribution of load in CMCs is very often equal between the matrix and reinforcement fibers, unlike metal or polymer matrix composites where the fibers usually bear the largest part of the loading. The main role of the reinforcements in ceramic matrix is to provide support to very brittle ceramic matrix that lack toughness, in order to arrest crack development and prevent catastrophic failures. Additional difference is related to chemical compatibility and thermal mismatch between ceramic matrix and reinforcements, because CMCs require very high temperatures for processing, and properties of each constituent have significant influence on possibility to form a composite, as well as on composite performance (Chawla, 2019).

Different reinforcements (fibers, whiskers, particulates, platelets) are used in CMCs, whereas each has different role in composite performance. Reinforcements need to be carefully selected, since lack of toughness and brittle ceramic matrix can provoke catastrophic failure at low strains ($<1\%$). Modeling and optimization of composite properties are very wide research area since it can direct and shorten the time for development of composite structure (Kojic *et al.*, 1996). Fiber reinforcements are especially important. There is a range of fibers that can be used in CMCs like alumina, silicon carbide, carbon, glass fibers, as well as novel hybrid fibers. In CMCs, unlike non-ceramic composites, fibers do not have the role to provide strength. Main role of fibers in CMCs is to provide toughness, whereas governing mechanisms are fiber debonding, fiber fracture and fiber pull-out. Interface between the matrix and the fiber is of the utmost importance, and very often includes certain thin layers of the third material that can provide appropriate strength of interfaces. Intermediate layer, at the interface between matrix and fiber, should have such bonding strength to enable load transfer but also debonding and pull-out of fibers, in case of cracking. Additionally, high temperature in processing and service of CMC components require optimal matrix – reinforcement combinations that must consider the following:

- (1) Temperature resistance,
- (2) Chemical compatibility and,
- (3) Thermal expansion mismatch.

First CMC composites, 60 years ago, had glass matrix and carbon fibers as reinforcement (Meetham and Van de Voorde, 2000). It was fabricated by impregnation of carbon fiber tows with glass powder in solvent that included organic binder. Prepreg sheets

were further produced by winding the tows. Dense composite were produced by hot pressing these prepreps in a graphite die. This CMC had improved strength and toughness, but corrosion resistance was not so good, due to oxidation behavior of carbon fibers. Some 20 years after this glass-carbon composite, SiC fiber commercially appeared, with significantly improved corrosion resistance. Very soon, SiC fibers in glass matrix were investigated for applications in jet engines and study indicated the need to increase range of temperatures that composites can withstand. Next, SiC/SiC composites (SiC fibers in SiC matrices) were fabricated, by using chemical vapor infiltration (CVI) processing route. However, SiC fibers did not have the same temperature capability as bulk SiC, which limited the temperature range of SiC/SiC composite up to 1100–1200°C that is much lower than the work temperature of sintered SiC (1650°C).

In general, one of the issues in CMC development is the lack of fibers that can withstand extremely high temperatures, beside the cost of CMC production. Also, intermediate layers between matrix and fibers are of the utmost importance for composite toughness and very often this third material disappears at very high work temperatures, what represents yet another issue to consider. Control and optimization of matrix/fiber interface is also the subject of research, as well as high-temperature fiber coatings. Phase control, defect tolerance and thermal shock resistance altogether determine the life and proper functioning of CMCs. Unlike metals, the major problem is non-existence of dislocation movement in ceramic structure, or lack of defect tolerance. Accordingly, CMC design must consider increase in defect tolerance. Design of components should consider that compressive strength of ceramics is very high, while tensile strength is very low. Ceramics do not exhibit plastic deformation, due to lack of dislocation movement, meaning that they cannot redistribute stress. Accordingly ceramics are highly sensitive to local stress concentrations that can originate from production, or functioning. Addition of fibers in ceramic matrix significantly increase defect tolerance. However, physical properties of constituents must also be considered in relation to thermal cycling, in order to increase thermal shock resistance of the composite, for those applications where the property is essential (e.g., turbine blades). Thermal shock resistance (resistance to a rapid cooling or heating) is defined as the temperature difference that might cause the failure under steady heat flow conditions (Hasselman, 1963). It is the resistance to failure that might originate from rapid cooling or heating. Rapid cooling is more dangerous for ceramics than heating, since it can induce a tensile stress which is more detrimental for ceramics that have low tensile stress tolerance. Thermal properties of ceramics are significantly influenced by reinforcing materials, as well as impurities, defects and porosity. For composite design, thermal expansion of each constituent must be considered because incompatible thermal behavior of two phases can induce complex stresses and lead to cracking, delamination or bowing of the composite. Properties of different CMCs can be found in the literature (Tressler, 2001; Chawla, 2019).

Physical properties of the matrix and fiber determine their thermal expansion so there must be a physical compatibility between them. Their chemical properties determine interface properties and must be designed considering all previously stated: well-designed bond between matrix and reinforcement to support both load transfer and fiber debonding, pull out and fracture. Under tensile load, ceramic matrix will crack first and if it is too strong, the failure will be brittle, without deflection, and will almost surely lead to catastrophic failure. Appropriate matrix/fiber interface will enable fiber debonding, fiber fracture and fiber pull-out, that will all act as energy absorbers and accordingly reduce the rate of crack development, as shown in Fig. 1. Continuous fiber reinforcement was the start of CMC development, but afterwards different forms of the second phase have been studied, including hybrid composite structures (both fibers and particles added as reinforcements). Among other roles, particles serve for crack deflection, since the crack path would follow particles distribution, as shown in Fig. 1. Nowadays, in CMCs, typical useful reinforcements (dispersed phase) are particles, platelets, whiskers and fibers (continuous, discontinuous, short, recycled), and extensive research is realised aiming at best composite properties, depending on its final functional application.

CMCs have been developed mainly to serve as high temperature materials, and many different aspects must be considered including environmental resistance, erosion, wear, mechanical behavior (mechanical, thermo-mechanical and corrosion fatigue,

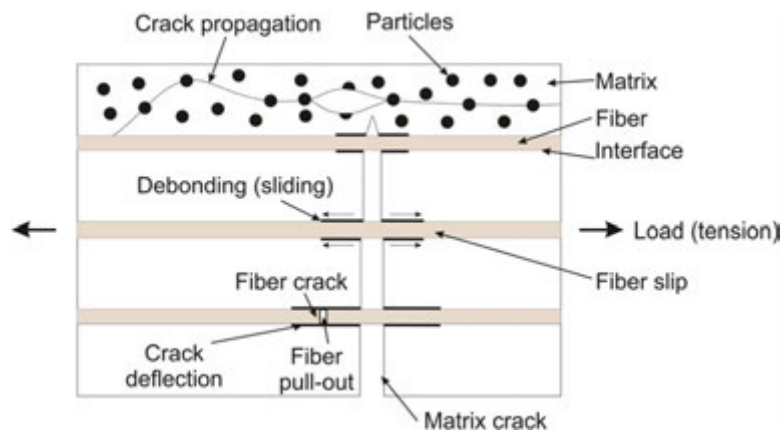


Fig. 1 Reinforcement mechanism for continuous fiber in brittle ceramic matrix (lower part of the image) and for particulate reinforcements (upper part of the image).

creep) beside physical properties (Meetham and Van de Voorde, 2000). Main requirement is to increase defect tolerance and reliability, followed by the requirement for increased temperature capability (for high temperature applications). However, recently, ceramic based composites have been widely considered in other fields like electronics or biomedical implants, where very high temperatures are not of interest during its work life. But thermal properties must be also considered in those areas, since the composite fabrication usually involves high temperatures.

Mechanical properties of composites are of the utmost importance for their performance. For the high-temperature ceramic, creep behavior is one of the key properties to ensure long-term performance. CMCs development was also aimed at creep resistance improvements. In composites, creep begins with a creep of matrix, but interactions with reinforcements (rigid or quasielastic) have significant influence on the composite behavior.

Structural integrity of elements is directly correlated with their fatigue behavior, associated with cyclic loading in extended time periods. Even so, experimental study of CMCs' fatigue behavior is largely lacking. For a long time, fatigue was discarded in CMCs since ceramics do not exhibit extensive dislocation movements, in general. However, numerous components made of CMCs are subjected to load fluctuations (disks, piston rings, turbine engines, etc.) and experience fatigue damage. Research on fatigue of CMCs indicated two general fatigue mechanisms: interfacial wear and generation of new flaws in fibers (Warren *et al.*, 2000). Frictional sliding at the matrix/fiber interface and viscous flow of glassy phases, especially at high temperatures determine fatigue related deformation properties. Fatigue fracture will occur for the stresses that are above the stress limit of the matrix. Forming of cracks is accompanied with debonding and reciprocating sliding of fibers along the matrix/fiber interfaces. Accordingly, fatigue is governed by the associated wear mechanisms and not just by the matrix and fiber material properties alone. Such interfacial wear results in decrease of fiber strength. Additionally, wear introduces damage in fibers and matrix at the matrix/fiber interfaces and furthermore decrease fiber strength. Some evidence points out that fiber strength can decrease up to 15%–30%, due to these processes (Warren *et al.*, 2000).

CMCs with oxide matrices are not susceptible to corrosion, in general, but for CMCs that have non-oxide matrices, oxidation and corrosive processes are very important since they can induce damage in a very short time. Different approaches have been used to overcome this issue for hostile environments, among which coatings are commonly applied. The most affected zones in CMCs are matrix/fiber interfaces. In case of carbon fibers, corrosion can completely remove the fibers from the matrix in a very short period. SiC fibers are also endangered by oxidation and important research has been realised to find optimal protective systems. One of the widely accepted approaches is to apply specific coatings on the fiber ($< 1 \mu\text{m}$ thickness), prior to CMC fabrication. On the other hand, such coating forms the thin interface layers between the matrix and fiber, and must be designed also to consider mechanical properties (e.g., provide load transfer). Development of fiber coatings that are both corrosion resistant and have adequate mechanical properties is rather recent and still needs research.

Microstructural stability of composites largely depends on compatibility of constituents, and must be seriously considered in material design. Interface layers between the matrix and reinforcement can provoke unwanted chemical reactions if they are not suitably selected and immediately compromise the integrity of the composite, or afterwards during operations. Beside the matrix and fibers, protective interface layers must also be considered. Altogether, this makes complex microstructural system even for two-phase composites, and in case of novel hybrid composites (with several types of reinforcements, like particles and fibers together), it is largely still under research.

Types of Ceramic Matrix Composites (CMCs)

CMCs are commonly grouped into two basic classifications: oxide and non-oxide composites, based on the matrix material. There is also general classification according to applications: aerospace and non-aerospace applications (energy, nuclear reactors, electricity and electronics, biomedical applications, etc.). Typical matrices and reinforcements in commercially used CMCs, or currently investigated, are shown in Table 1. Group of biomedical CMCs are included as a separate group, since these represents rather recent state-of-the-art research.

Different reinforcements are used, whereas particulates and fibers are among the most common ones, but numerous other forms of reinforcing phases have been the subject of study, such as whiskers, platelets, micro- and nanoparticles, micro- and nanotubes (e.g., carbon nanotubes, CNT). There are many already applied particulate reinforcements (SiC, TiC, TiN, TiB₂, Al₂O₃, ZrO₂, TiB₂, B₄C, BN, etc.); fibers (C, SiC, Al₂O₃); platelets (graphene, SiC, Al₂O₃, Si₃N₄); whiskers (B₄C, Si₃N₄, SiC, Al₂O₃), including novel nanostructures (graphene, CNTs). Reinforcing fibers can be in a form of continuous fibers, discontinuous (short, long, whiskers; uniformly or randomly distributed, unidirectional or with predesigned pattern), or recycled fibers as one of the important current research area. Carbon fibers are among the most used fibers. Carbon is a very light element and can exist in many forms (allotropes), whereas for carbon fibers that are used in composites, carbon has graphitic structure (carbon atoms are arranged in hexagonal layers). New carbon form is graphene, which is usually added in a form of platelets, but also as thin layer to represent interphase material in hybrid composites. Another novel form of carbon is CNT, usually added as small amount of nanoparticles. Composite combinations of reinforcements are also used, as recent research trend in development of hybrid composites.

Silicon carbide (SiC) is an engineering ceramic that combines strength and chemical inertness with high temperatures resistance. SiC is very stable also in environments with high radiation (Katoch *et al.*, 2014). There are many polymorphic forms of SiC. Silicon carbide came into attention as ceramic for composite matrix material because of its excellent oxidation resistance, corrosion

Table 1 Typical matrices and reinforcements in CMCs and research areas (references)

Matrix	Reinforcement	References
Oxide matrices		
Al ₂ O ₃	Ni, TiC, Al ₂ O ₃ ZrO ₂ , SiC, t-ZrO ₂ , m-ZrO ₂ , Ni, graphene, TiN	(Zygmuntowicz <i>et al.</i> , 2019; Ahmed <i>et al.</i> , 2017; Lü <i>et al.</i> , 2019; Mebrahitom Asmelash and Mamat, 2012; Sarraf <i>et al.</i> , 2008; Wolff <i>et al.</i> , 2019; Balinova <i>et al.</i> , 2018; Zhou <i>et al.</i> , 2020a; Huang and Wan, 2020; Nieto <i>et al.</i> , 2017; Liu <i>et al.</i> , 2013; Hou <i>et al.</i> , 2021; Liu <i>et al.</i> , 2020b)
Al ₂ O ₄	Ni	(Zygmuntowicz <i>et al.</i> , 2018)
SiCO	TaSi ₂ , MoSi ₂ , ZrO ₂	(Li <i>et al.</i> , 2018; de Almeida Silva <i>et al.</i> , 2020)
SiO ₂	Al ₂ O ₃ , SiC, ZrO ₂	(Chengxin <i>et al.</i> , 2019; Boccaccini, 2001; Balinova <i>et al.</i> , 2018)
ZrO ₂	Ni, Al ₂ O ₃ , HA, MgAl ₂ O ₄	(Zhou <i>et al.</i> , 2015; Abdullah <i>et al.</i> , 2012; Wong <i>et al.</i> , 2002; Mebrahitom Asmelash and Mamat, 2012)
Non-oxide matrices		
SiC	SiC, SiC-fiber, Tyranno ZMI, Tyranno SA ₃ , B ₂ O ₃ , Al ₂ O ₃ , TiB ₂ , PCF, C, Al ₂ O ₃ -Y ₂ O ₃ , Al ₂ O ₃ -Y ₂ O ₃ + additives (MgO, CaO, TiO ₂ , La ₂ O ₃ and SiO ₂ from the oxide group, TiC from carbides, TiB ₂ and ZrB ₂ from borides and AlN and TiN from nitrides), Al ₂ O ₃ -Y ₂ O ₃ -MgO, Al ₂ O ₃ -Y ₂ O ₃ -CaO, Al ₂ O ₃ -Y ₂ O ₃ -TiO ₂ , Al ₂ O ₃ -Y ₂ O ₃ -La ₂ O ₃ , Al ₂ O ₃ -Y ₂ O ₃ -SiO ₂ , Al ₂ O ₃ -Y ₂ O ₃ -TiC, Al ₂ O ₃ -Y ₂ O ₃ -TiB ₂ , Al ₂ O ₃ -Y ₂ O ₃ -ZrB ₂ , Al ₂ O ₃ -Y ₂ O ₃ -AlN, Al ₂ O ₃ -Y ₂ O ₃ -TiN, graphene, Cf/ZrB ₂	(Shimoda and Hinoki, 2021; Whitlow <i>et al.</i> , 2019; Mansour and Morscher, 2019; Kollins <i>et al.</i> , 2018; Borkowski and Chattopadhyay, 2015; Xu <i>et al.</i> , 2015; Wrbanek <i>et al.</i> , 2012; Geetha <i>et al.</i> , 2009; Nakayama <i>et al.</i> , 2019; Lee <i>et al.</i> , 2013; Quemard <i>et al.</i> , 2007; Naslain <i>et al.</i> , 2004; Naslain, 2004; Mogilevsky and Zangvil, 2003; Katoh <i>et al.</i> , 2014; Zhu <i>et al.</i> , 2002; Li, 2018; Ye <i>et al.</i> , 2019; Whitlow <i>et al.</i> , 2019; Mori <i>et al.</i> , 2017; Ikarashi <i>et al.</i> , 2019; Schönfeld and Klemm, 2019; Khodaei <i>et al.</i> , 2019a,b; Naslain, 2005; Katoh <i>et al.</i> , 2014; Sabahi Namini <i>et al.</i> , 2015; Zhou <i>et al.</i> , 2020a; Huang and Wan, 2020; Nieto <i>et al.</i> , 2017; Makurunje <i>et al.</i> , 2021; Zhang <i>et al.</i> , 2020a; Liu <i>et al.</i> , 2020a; Adibpur <i>et al.</i> , 2020)
N720	Al ₂ O ₃	(Presby <i>et al.</i> , 2019)
C	C-SiC, C, SiC	(Chen <i>et al.</i> , 2018a; Besra and Liu, 2007; Lee <i>et al.</i> , 2013; Naslain, 2005; Yang <i>et al.</i> , 2020; Shen <i>et al.</i> , 2019; Mikociak <i>et al.</i> , 2018)
ZrB ₂	C-fiber, MoSi ₂ , HfSi ₂ , WSi ₂ , ZrC-rods	(Silvestroni <i>et al.</i> , 2019; Cheng <i>et al.</i> , 2017)
Si-B-C	SiCf	(Maillet <i>et al.</i> , 2014)
Ca ₂ O ₄ Si	SiC, SiC-fiber	(Haertling, 1999; Gao <i>et al.</i> , 2015)
Zr	ZrC	(Nakayama <i>et al.</i> , 2019)
SiCf	Si-B-C, SiC, Al ₂ O ₃	(Godin <i>et al.</i> , 2016; Zhang <i>et al.</i> , 2017)
SiCN	C, Pd ₂ Si, Fe, Co	(Bakumov <i>et al.</i> , 2012; Zaheer <i>et al.</i> , 2011; Hauser <i>et al.</i> , 2008)
B ₄ C	B ₂ O ₃	(Naslain <i>et al.</i> , 2004)
GIC	HA	(Najeeb <i>et al.</i> , 2016)
TiB ₂	SiC	(Sabahi Namini <i>et al.</i> , 2015)
BN	m-ZrO ₂ , MgO, Al ₂ O ₃ , TiO ₂	(Eichler and Lesniak, 2008; Chen <i>et al.</i> , 2018b)
AlN	h-BN, graphene	(Cho <i>et al.</i> , 2006; Zhou <i>et al.</i> , 2020a; Huang and Wan, 2020; Nieto <i>et al.</i> , 2017)
Bioceramics		
HA	C, SiC, CuO, Alginate, PLGA, CaSiO ₃ , TZP	(Zhao <i>et al.</i> , 2021; Hosseini <i>et al.</i> , 2021; Wu <i>et al.</i> , 2021; Mahmoud <i>et al.</i> , 2020; Kim <i>et al.</i> , 2006a,b; Papynov <i>et al.</i> , 2020; Kong <i>et al.</i> , 1999)
CaP-based	Polymers (PEG, PAA, PLGA, PGA, PCL, PLLA, etc.), Collagen, Graphene, Mullite, Ce, Ti	(Wagoner Johnson and Herschler, 2011; Santos <i>et al.</i> , 2008; Eliaz and Metoki, 2017; Zhou <i>et al.</i> , 2012; Priya <i>et al.</i> , 2010; Sousa <i>et al.</i> , 2020; Lewin <i>et al.</i> , 2020)
Bioglasses (SiO ₂ , CaO, Na ₂ O, P ₂ O ₆ , Si ₃ N ₄ , MAS)	SiC, C, Ni-Si-B alloy,	(Opila <i>et al.</i> , 2016; Deng <i>et al.</i> , 2018; Ishikawa, 1994; Ahn and Mall, 2009; Zhang and Hayhurst, 2011; Kastritseas <i>et al.</i> , 2010; Chawla <i>et al.</i> , 2001)

resistance, and low density even at high temperatures (Florian *et al.*, 2011). Nanostructured SiC has shown some exceptional properties (Matovic *et al.*, 2016). These materials have found their application in engineering and chemical industries. Major drawback of pure SiC is its brittleness and it is significantly improved in composites with SiC matrix (Kohyama *et al.*, 2006).

SiC/SiC composites provide exceptional increase in fracture toughness, thermal shock resistance and flexural strength compared to pure SiC (Kohyama *et al.*, 2006). SiC based composites extended application of pure SiC to high temperature wear parts such as seals, sleeves, bearing balls, armor, cutting media and other (Florian *et al.*, 2011). They are also used for wear and corrosion resistant components at low temperatures, such as sandblasting injectors, automotive water pump seals, bearings, pump

components, and extrusion dies. Strength and toughness of SiC can be improved by whisker, particle or fiber reinforcements (Shimoda and Hinoki, 2021). Common fiber reinforcement materials are Hi-Nicalon, Tyranno SA and carbon. These types of composites showed crack propagation along the two phases interface, because the reinforcements are smooth and provide low frictional forces and easy crack propagation (Florian *et al.*, 2011). Boron nitride and silicon carbide interfacial coatings in SiC/SiC composites showed that double-layered BN/SiC-2 can provide crack deflection between the sublayers and also at BN/fiber interface (where fibers debonded) (Dai *et al.*, 2020).

C/SiC composites have found their role in automotive and railway industries as materials used for friction plates, brake disks, brake pads; in aerospace industry they can be found in gas turbines, rocket engines, thermal shields; in satellites as structural components; in microelectronics as cooling components; in energy industry as heat exchanging assemblies, in nuclear power plant components; in protection systems in ballistics (Hofbauer *et al.*, 2019). New hybrid forms are studied, such as (Hf,Ti)C-SiC ultra-high temperature composite (Makurunje *et al.*, 2021). Also, tailoring of the SiC ceramics through design of the fibers, matrix and matrix/fiber interphase, as well as suitable coatings can provide SiC-based composites with specific functions, like self-healing, microwave shielding or self-lubrication (Yin *et al.*, 2017).

Alumina is one of the strongest ceramics with very high hardness, high melting point at 2040°C, high abrasion and wear resistance. There are multiple forms of alumina, but only the hexagonal alpha-alumina is stable at high temperatures. Alumina is practically insoluble in any solvent at a physiological pH level. It is bioinert and highly chemically stable. Due to cracks and voids, it can be susceptible to impact forces, which is why it is often mixed with additives, to create alumina-based CMCs. It is often used as a ceramic component in cermets (metal/ceramic composites) and as reinforcement in metal matrix composites (Babić *et al.*, 2011, 2010). Alumina is used for joint replacements, dental implants, femoral heads and other orthopedic applications (Cardarelli, 2018; Murphy *et al.*, 2016; Hasirci and Hasirci, 2018).

Zirconia is dense polymorphic bioceramic with high mechanical strength and fracture toughness. It can exist in a form of monoclinic zirconia with a density of 5850 kg m⁻³ at temperatures up to 1197°C, when it transforms into a tetragonal phase, that is stable up to 2300°C. Tetragonal zirconia (6045 kg m⁻³) transforms into cubic zirconia with lower density (5500 kg m⁻³). Cubic zirconia melts at 2710°C. These phase transformations are very important because, as density values show, significant volume changes can occur, and cause cracks in the material. Therefore, pure zirconia is not resistant to thermal shocks and needs to be stabilized, by adding oxides such as MgO, CaO, Y₂O₃, CeO₂ and La₂O₃ of which calcium oxide (CaO) is the most commonly used one. Zirconia can be partially or fully stabilized and stabilized forms are generally tetragonal or cubic. Temperature changes would then cause microcracks to appear, which would dissipate the energy from propagating cracks and slow their propagation. Also, partially stabilized zirconia has a transformation toughening mechanism that is connected to the tetragonal-monoclinic phase transformation. Zirconia-based ceramics have shown low friction and high wear resistance, useful in orthopedic applications such as joint replacements, bone screws, artificial knees, maxillofacial reconstruction, dental crowns and bridges (Cardarelli, 2018; Murphy *et al.*, 2016; Hasirci and Hasirci, 2018). Due to its phase transformation, some recent research is aimed at self-healing properties, like in ZrB₂-ZrC-SiC-ZrO₂ ceramics (Dedova *et al.*, 2019).

Zirconia-Toughened Alumina (ZTA) is developed, by adding zirconia (ZrO₂) to alumina (Al₂O₃), to improve fracture toughness and wear resistance of alumina, which is otherwise a very affordable ceramic material. Along with zirconia, small amounts of yttria (Y₂O₃) are also added for stabilization. These additives improve fracture toughness and resistance, by inhibiting crack propagation. Deforming the tip of the crack by blunting it consumes energy and slows down crack propagation, resulting in improved fracture resistance. Crack resistance can also be improved by introducing compressive residual stress that result from different thermal expansion coefficients of zirconia and alumina in multi-layered composites with different contents within inner and outer layers. Depending on the preparation method and technology, ZTA can have very high porosity and low density. Although it improves toughness, zirconia has a higher density and lower hardness values, as well as lower elastic modulus. Amount of zirconia in ZTA is also limited due to its higher cost. Pure alumina is more favorable for high temperatures and stresses. Under elevated temperatures, ZTA's toughness decreases quickly and if the temperature rise is cyclically repeated ZTA exhibits thermal fatigue. Some of ZTA applications are ballistic armor, petrochemical and chemical equipment and equipment used in otherwise corrosive environments, metal cutting tools subjected to high temperatures, lightweight insulation materials, and artificial joint replacements and bone implants (German, 2016; Chen *et al.*, 2018a). Also, new hybrid composites with W and WB particles have been investigated (Bazhin *et al.*, 2021).

Al₂O₃/Ni composite is suitable for making gradient structures of high density in the shape of hollow cylinders. Nickel particles are introduced into the ceramic matrix for their ductility to improve the overall fracture toughness of the composite. Even though this composite material has higher fracture toughness than monolithic ceramics it is still very brittle. The percentage of nickel phase changes through the volume of the material and so do the mechanical properties of the composite, i.e., alumina-rich zones have higher hardness values. Since the highest stresses appear on the surface of the sample, that is where the highest concentration of nickel additive is needed (Zygmuntowicz *et al.*, 2019; Zygmuntowicz *et al.*, 2018).

Al₂O₃/TiC composite is characterized by high density, hardness and wear resistance. It also possesses good flexural strength. Other additives can be added to the composite, such as zirconia and iron powder, to improve fracture toughness but their addition can further increase porosity and worsen other mechanical properties. Application for this material can be found in the development of new high-speed machining tools (Ahmed *et al.*, 2017).

Al₂O₃ anisotropic grain growth (AGG) is used to toughen pure alumina that lacks ductility. This problem is addressed by alloying it with certain additives that can toughen it. One of the strategies employed is achieving an anisotropic grain growth (AGG). Sintering does not induce grain growth anisotropy in pure alumina. Adding oxides such as La₂O₃ or Nb₂O₅ facilitates dynamic

grain growth and helps form an interlocked microstructure with columnar grains in certain directions, thereby toughening the material (Lü *et al.*, 2019).

Al₂O₃/SiO₂ high strength composite is created by adding alumina (Al₂O₃) to silica (SiO₂) matrix. This composite is very resistant to elevated temperatures and thermal shock cycles. This, along with lower density than metals, makes it an attractive option for aerospace engineering applications. Composite is stable at high temperatures, and also resistant to oxidation. It can maintain good properties such as high flexural strength and low density, and exhibit ductile fracture up to a very high temperatures, above 1000°C.

Silica (SiO₂) is a suitable matrix for high temperature CMCs due to its own resistance to thermal shocks, as well as good chemical and mechanical stability. Silica-based composites have found applications in various demanding environments such as aeroengine combustion chambers, spacecraft components, helicopter exhausts etc. (Chengxin *et al.*, 2019).

Hexagonal boron nitride (h-BN) is important ceramic due to its properties: high chemical and electrical resistance, also in corrosive environments and high temperatures, thermal stability and heat shock resistance (Chen *et al.*, 2018b). High purity pyrolytic h-BN has excellent mechanical and thermal properties at high temperatures, but at the same time it resembles the graphitic structure in being soft and easily worked. Composites with boron nitride matrices, with different reinforcements (fibers like Nicalon (SiC), Al₂O₃, Al₂O₃-SiO₂) are used in versatile areas (cosmetics, automotive industry, thermal management systems, etc.). Some of the components where it is used are seals for acid sensors, components in high temperature furnaces, containers for molten glass and aluminum. The electrical resistance can be adjusted by the h-BN/TiB₂ composition. BN/m-ZrO₂ composite is favorable for wear resistant components at elevated temperatures that require high-temperature compressive strength (Eichler and Lesniak, 2008).

TiB₂-based ceramics have high melting point, high modulus of elasticity, high hardness and high resistance to abrasion and make them suitable for use under extreme loads. TiB₂ ceramics exhibit good wetting of liquid aluminum and high corrosion resistance to the molten salt of cryolite, which makes it suitable as cathode material in aluminum electrolysis. However, full densification of the composite is difficult and requires both high temperature and high pressure (SiC/TiB₂). Different approaches have been studied including non-pressure sintering, hot pressing and spark plasma sintering (Sabahi Namini *et al.*, 2015).

Aluminum nitride (AlN) is used in electronics and optics, since it has excellent thermal conductivity and optical properties. It has similar thermal expansion coefficient as silicon. AlN is sintered with h-BN particles to form high temperature CMCs (Cho *et al.*, 2006).

Molybdenum disulfide (MoS₂) has chemical and thermal stability. It can form very efficient dry lubricating film and is widely used in tribological applications. MoS₂ particles within ceramic matrix (e.g., alumina) act as solid lubricant, due to their low friction coefficient, good catalytic activity, high reactivity, and increased adsorption capacity compared to the bulk material. They can be produced by several electro-chemical routes. *Molybdenum dioxide (MoO₂)* is also added as filler to CMCs, like alumina-zirconia composite, in order to provide surface strengthening and to act as dry lubricant and conductive filter (Li and Zhu, 2015).

Application Areas of Ceramics and Ceramic Matrix Composites

Applications of ceramics and ceramic-based materials are wide, but high cost primarily limits their use. On the other hand, many ceramic materials are not observed as ceramics, making this research area apparently smaller than it really is. Usually, CMCs are grouped in aerospace applications and other fields. Aerospace applications have been the most influential drive of CMCs development and research and they still are, because CMCs offer specific benefits in material properties that a material must satisfy in aerospace components, like:

- (1) Simultaneously providing low weight and high strength and stiffness (important for reduced fuel consumption);
- (2) Possibility to operate at very high temperatures, thus increasing thermal efficiency;
- (3) Long functional life.

Production and maintenance costs altogether have justified the high cost of CMCs in aerospace applications. Environmental footprint of the life cycle of ceramics and CMCs are not known, especially in terms of energy consumption, even though involved processing is very energy intensive.

Other important application areas of CMCs include cutting tool inserts, filters, heat engines, energy conversion and storage devices, military systems, nuclear reactors, components working in hostile environments (like turbine blades), and electronic/electrical applications (Chawla, 2019). Some other areas do not consider that ceramic composites are used, even though they are indeed ceramic composites, like refractories, which are high-temperature resistant materials. Refractories are made from powder mixtures of different constituents (oxide ceramic powder, graphite flakes, and polymer resins), with large distribution of particle sizes that enable efficient densification through shape forming processes and firing, unlike sintering. Consumption of refractories is very high since they are heavily used in iron and steel industry, glass melting, ceramic and cement industries (Warren *et al.*, 2000). Another exceptionally large consumption of CMCs is related to concrete and cement industries. Cement production and use are among the largest industries in a world. Some statistics indicate that around 4 billion tons of cement (key constituent of concrete), is produced per year, with constant yearly increase of consumption. Research efforts related to cement and concrete compositions and processing routes are aimed at replacing cement in concrete and lowering CO₂ emissions, since this industry accounts for around 8% of global CO₂ emissions.

Cutting tool inserts are heavily used in production industries worldwide and any energy and cost savings considering their consumption result in enormous savings. Performance of CMCs in this field has shown significant improvements (e.g., silicon carbide whisker reinforced alumina, $\text{SiC}/\text{Al}_2\text{O}_3$), in comparison to standard inserts, from aspects of fracture toughness and strength, as well as thermal shock resistance. Accordingly, CMCs can introduce significant prolongation of functional life of cutting tools.

Ceramics are usually observed as electrical insulators and majority of them are. However, many ceramics can conduct electricity and some of them even are superconductors. Al_2O_3 and ZnO are insulators, but in some forms, ZnO can be n-type semiconductor (impurity semiconductor). $\alpha\text{-SiC}$ and AlN are semiconductors. In general, ceramics have the broadest range of electrical properties of all material classes, with complex conduction mechanisms and electrical conductivity over broad value ranges (Carter and Norton, 2013). Some ceramics (e.g., BaTiO_3) have positive temperature coefficient (related to temperature coefficient of resistivity and electron mobility). Barium titanate (BaTiO_3) is a prototypical perovskite ferroelectric material (Nowotny and Rekas, 1994; Erhart and Albe, 2008). SiC is wide-band-gap semiconductor that is used in sensors that work in hostile environment and high temperatures up to 600°C (aircraft, fuel cells), instead of standard electronics (Carter and Norton, 2013). Main applications for conductive ceramics are resistors and electrodes.

The first magnets used by humans were made of ceramics, even though magnetism is usually associated with metals. Nowadays, more than half a million tons of ceramic magnets are produced each year, where permanent magnets made of hard ferrites (based on Fe_2O_3) account for the largest part. Ceramic magnets are used for electric toothbrushes (motors), door seals (refrigerator), back stripes on credit cards, in mobile phones, etc.

Heat affects ceramic properties and many applications utilize this, such as in high thermal conductivity substrates for electronic packaging. Glass-ceramics can have ultra-low thermal expansion coefficient (e.g., lithium-alumino-silicates) what is favorable for applications such as supports for telescope mirrors, aiming to minimize thermally induced strains.

In energy production and storage, ceramics are applied in critical components in solar cells. For example, TiO_2 is used in dye-sensitized solar cells as the support structure. Li-ion battery cells have one of the highest energy densities of any battery technology today, which is enabled by the ceramic mineral structures (olivine).

Very interesting ceramic material is zeolite (aluminosilicate minerals) and zeolite-based composites, which are microporous and used as absorbents, catalysts and filters at micro and nano scales. Composites such as SiC matrix reinforced by different ceramic fibers have important application in filtration at very high temperatures up to 1000°C . High temperature capability of these filters eliminates the need for the pre-filter cooling and makes significantly more efficient and less complex system. This is very useful for heat exchangers and applications can include combustion, gasification and incineration systems (Chawla, 2019).

Carbon fiber-reinforced silicon carbide (C/SiC) CMCs are among the most famous composites for high-temperature structural applications, such as jet engines in aircrafts, sharp leading edges, thermal protection systems in vehicles, optical components, and nuclear reactors, due to significantly improved fracture toughness and thermal shock resistance (Zhang *et al.*, 2018).

Bioceramics

Extracellular matrix (ECM) is found in tissues and supports cell proliferation and differentiation. Artificial scaffolds should mimic ECM in a way to provide micro scale topographies and biochemistry good enough for regulation and control of cell and tissue behavior. Also, scaffolds should mimic the micro- and macro-structure of a natural bone. These features combined can provide space for new cells and tissue growth. Mechanical properties, stiffness, strength and mechanical behavior of the scaffold should be close to those of the natural bone tissue (that have Young's modulus in a range of 1–27 GPa). New biomaterials have introduced degradation as beneficial property for certain scaffolds. Degradation rate should be optimal, since high values can result in premature scaffold failures. Design of composites must consider the biocompatibility along with all other properties (Wu *et al.*, 2014). Ceramics have important role in diverse biomedical applications. For example, one of the most used bioglass is Poly (methyl methacrylate) (PMMA). Even though it is widely used, there are still some aspects that are under study, like tribological aspects, or the influence of porosity on fatigue stress behavior in vivo, or the influence of small nano and micro-sized particles on the surrounding tissues, as well as on the wear of metal implant surfaces (Zivic *et al.*, 2012, 2013).

Bioceramics comprise glass ceramics and calcium phosphates and more recent bioactive ceramics and bioglasses (bioactive and bioresorbable), that have been developed during the last decades (Li and Zhitomirsky, 2020; Floroian *et al.*, 2015; Durgalakshmi and Balakumar, 2014; Magnan *et al.*, 2013; Best *et al.*, 2008). The main advantage of bioceramics is their biocompatibility, together with low density and wear resistance. One of the most used ceramics, alumina is chemically inert and biocompatible, but lacks the ability to directly bond with a bone. Both alumina and zirconia, as high strength materials, are widely used in orthopedic implants. Some statistics indicate that more than a million alumina components for hip joint replacements have been implanted. The main disadvantage of high strength ceramics is related to low toughness and very high modulus of elasticity that results in stress shielding. Other issues related to bioceramics are low tensile strength and high production costs. Stress shielding occurs for the tight contact of two different materials, when the material with significantly higher strength (ceramics in this case) bears all the loading of the system and weaker material (living bone) is shielded from the loading. For example, it would occur if artificial hip implant would be made of pure solid Al_2O_3 ceramic. In the long run, this is detrimental for living cells, since the cells need some degree of continuous load to maintain healthy state. This is one of the reasons that bioinert ceramics, like alumina (Al_2O_3), is usually coated with some other biomaterial, or investigated as composites. Alumina is used in joint replacements (knee, ankle, fingers, wrists, elbows, shoulders). Current bioceramics also include zirconia (ZrO_2), zirconia-toughened alumina (ZTA), alumina matrix composites (AMC), alumina-toughened zirconia (ATZ), silicon nitride (Si_3N_4), and hydroxyapatite (HA) (McEntire *et al.*, 2015).

Zirconia toughened alumina ceramics (AMC, ZTA, ATZ) contain Al_2O_3 matrix and refers to composites with alumina matrix (AMC) and zirconia-toughened alumina (ZTA). ZTA usually has 7–25 wt% ZrO_2 or yttrium-stabilized tetragonal zirconia (Y-TZP) dispersed in Al_2O_3 matrix. AMC is special case of ZTA with 24 wt% ZrO_2 and 1.7 wt% oxides mixture (Y_2O_3 , Cr_2O_3 , SrO). AMC has become the most popular orthopedic ceramic for articular implants. Alumina-toughened zirconia (ATZ) is completely dense ceramic that also contain Al_2O_3 and ZrO_2 (80 wt% Y-TZP and 20 wt% Al_2O_3). Zirconia toughened alumina ceramics have outstanding strength, toughness, and hardness, and are highly wear and abrasion resistant, due to transformation toughening (McEntire *et al.*, 2015).

Graphene platelet (GPL)-reinforced alumina (Al_2O_3) ceramic composites are new composites, where minor addition of GPLs efficiently improves the fracture toughness as well as flexural strength of alumina. However, hardness decreases with addition of GPLs. It is also shown that GPL/ Al_2O_3 composites have excellent biocompatibility with osteoblasts, but only in relation to flat faces of GPLs. Porosity and sharp GPL edges can inhibit cell proliferation. Pure Al_2O_3 ceramics exhibit an intergranular fracture mode, while GPL/ Al_2O_3 composites show both intergranular and intragranular fracture modes. GPLs show good distribution in composite when mixed with ceramics (Liu *et al.*, 2016; Liu *et al.*, 2015).

Bioactive ceramics have been developed to overcome the issue of chemical inertness, along with their composites that allowed tailoring of the modulus of elasticity, according to the surrounding tissues. One of the largely investigated bioactive ceramics is hydroxyapatite (HA) with similar structure as the mineral part of teeth and bones. Bioactive materials are those that interact with surrounding tissues at the interface, thus resulting in firm bonding between the artificial material and the living tissue. However, all known bioactive ceramics do not have high strength and cannot be used as load bearing elements in their pure forms. Accordingly, they are usually applied as coatings to provide the bonding with tissue, such as bioactive glass coating on metal. One of the first composites was the Bioglass® 45S5/AISI 316L stainless steel. It was made by infiltration of molten glass to the preform made of discontinuous metal fibers, followed by the specific heat-treatment (Carter and Norton, 2013).

Bioactive glasses have superb osteoconductivity, controlled biodegradability, cell delivery capabilities, the capacity for activation of osteogenic gene expression, good formation of bone mineral-like phases and have drug delivery abilities. Porosity can be designed in a range of 20%–80%, and Young's modulus in 1.2–83.4 GPa (Wu *et al.*, 2014). They potentially represent the most successful candidate for biomedical scaffolds. However, their mechanical properties still need improvements, because they are still brittle and do not have superelastic performance as natural bones. Mechanical properties significantly depend of processing routes, along with the structure of source materials.

Calcium phosphate (CaP) is a natural constituent of teeth and bones and its ceramics have the properties necessary for orthopedic applications such as bioactivity and osteoconductivity. In general, bioactivity refers to the ability of the material to interact with living tissue and body fluids, reacting with their ions. This result in the attachment of the cells guided over the surface of the CaP bone implant. This process is referred to as osteoconduction. Calcium phosphate bioceramics have been combined with certain metals such as titanium (Ti) to improve the load-bearing properties of the artificial bone scaffolds aimed for hip replacements. Ti-fiber-reinforced bioactive glass and ZrO_2 -reinforced A-W glass are some of the recent bioceramic composites (Carter and Norton, 2013).

CaP based composites can be tailored as biodegradable materials, but this is still under investigations. Related research results are inconclusive in relation to biodegradation rate of CaPs. It is still considered to be considerably slower than bone ingrowth, due to which they would remain in the body longer time than needed (Hasirci and Hasirci, 2018; Murphy *et al.*, 2016; Khan and Laurencin, 2018; León and Jansen, 2009). Tricalcium phosphate (TCP) is used in orthopedics and as dental material. It is a resorbable bioceramic that is replaced by the tissue as it resolves within it over time. They act as bone grafts, that is, scaffolds which enable cell proliferation and growth of new tissues. TCP cannot bear load due to low mechanical strength. Therefore, it is usually applied as coating on metals.

Calcium hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_5(\text{OH})_2$, or commonly known as hydroxyapatite (HA) is commonly used CaP bioceramic. HA crystals are impure and contain carbonate. It is known for being the mineral component of bone and dentin and having bone-bonding properties (osteoconductivity), meaning it induces bone cell (osteoblast) adhesion and proliferation to bridge the gaps between the implant and bone. The problem with this material is its low tensile strength, making it brittle. It is not suitable for high tensile stresses and cannot be a load-bearing material. Another drawback is that it does not exhibit any significant biodegradation. On the other side, this can be beneficial for some applications, like facial fillers for wrinkles. Bone-bonding and bioactive properties of HA and other CaP ceramics have over the years resulted in many applications in orthopedic treatments for damaged and diseased bones and orthopedic surgery, as well as maxillofacial surgery, repairing dental defects, spinal grafts and ocular implants (Hasirci and Hasirci, 2018; Murphy *et al.*, 2016; Khan and Laurencin, 2018; León and Jansen, 2009).

Hydroxyapatite was introduced in granular, dense, and porous forms in various therapies for bone defects, as tooth repairs and replacements, alveolar ridge augmentation, maxillofacial reconstruction, ossicles bone repair, as orbital implants, spinal fusion devices, and bone scaffolds. Early success of HA in dental procedures resulted in later use as coatings onto femoral stems and cups in total hip arthroplasty. Nowadays, hydroxyapatite is extensively used in bone implants that does not bear load. In physiological fluids, HA act as active material that promote formation and growth of bone cells and bonding with artificial implant (McEntire *et al.*, 2015).

Hydroxyapatite-based composites have higher mechanical strength, due to reinforcement phases that can be ceramics, polymers or metals. Addition of zirconia enhances fracture toughness, as well as bending strength. Mechanical strength and fracture toughness of HA ceramics can be increased by introducing short stainless steel fibers, even though that is not favorable from aspect of corrosion related reactions. HA can be mixed with collagen to create a bone-like composition, but tensile strength and modulus of elasticity are still not adjusted to requirements. HA-polyethylene composites have better mechanical properties,

but bioinert polyethylene doesn't promote bonding with living tissue (Orlovskii *et al.*, 2002). Hydroxyapatite – carbon nanotubes (HA-CNT) composites are relatively new materials. Limited tests that were conducted related to Young's modulus and hardness have shown that these values increase as CNT weight ratio increases, as well as compressive strength. Small additions of CNTs in HA, have significantly improved the strength and toughness of HA, without influencing its bioactivity (White *et al.*, 2007).

Composite biomaterial based on hydroxyapatite (HA), sodium alginate (Alg) and chlorhexidine (CHX) can be used as carrier system for local drug delivery, especially in dental procedures, since CHX is widely spread in dental medicine as an antibacterial and antifungal substance. HA also interacts with biomolecules and can serve as drug carrier, and can be used to enhance the remineralization of teeth. Low cost Alg exhibit excellent biocompatibility, biodegradability and also has potential in drug delivery systems. Accordingly, their combination has been investigated for drug delivery systems. It is important that processing routes significantly influence the final composite properties. Adsorption and release rate of CHX depend on processing temperatures (dried at 37°C, lyophilized at –55°C and annealed at 1100°C). The increase of Alg content reduces the size of HA crystals, increases composite deformability, swelling, and porosity (Sukhodub *et al.*, 2018).

Dental ceramics have been used for dental restorations for more than 200 years, such as feldspathic porcelain (based on feldspar ceramic). Low fracture toughness of ceramics, especially under very low strain (0.1%) is one of the major problems, which is solved by different material modifications, including ceramic composites. Nowadays, CMC composites for dental applications with improved properties have been obtained by reinforcement of glass matrix by different particles, such as alumina, leucite, spinel. Leucite, KAlSi_2O_6 , is a mineral (feldspathoid group with low silica content) and its addition improves thermal expansion coefficient. Spinel, MgAl_2O_4 , originates from metamorphic mineral and has cubic crystal system.

Carbon and Carbon Based Composites

Carbon is a chemical element that can exist in several allotropic forms, depending on its crystal structure: graphite where carbon atoms are in hexagonal layers (the most stable allotrope); three-dimensional diamond structure (diamond cubic); and several newly discovered crystal structures like graphene (single layer of graphite), amorphous carbon (without any crystalline structure), single-walled carbon nanotube (SWCNT), multi-walled carbon nanotubes (MWCNTs), buckminsterfullerene (C_{60} , ball shape – buckyball) and many other forms. For composites, four graphite forms are currently interesting: pure graphite (carbon fiber graphite), CNTs, graphene and pyrolytic graphite. Carbon fiber graphite and pyrolytic graphite, with glassy isotropic structures, have exceptional strength and heat resistance up to 3000°C.

Carbon fiber is a form of graphite, where graphitic layered structure is arranged in long thin sheets, whereas these ribbons of graphitic sheets are packed together to form fibers that are exceptionally strong. Properties of these fibers (size, orientation, height) can be modified to provide desired final properties (Chawla, 2019; Morrell, 2000; Bunsell and Berger, 2000). Carbon fibers, as composite reinforcements, are extensively used in many structural applications today.

Carbon nanotubes (CNTs) are carbon tubes with nano-scale diameters. They are commonly used as single-walled carbon nanotubes (SWCNTs), and multi-walled carbon nanotubes (MWCNTs). MWCNTs consist of nested SWCNTs that are held together by weak van der Waals interactions (tree ring-like structure). Physical properties and behavior of CNTs in ceramic matrix composites are still under study (Rivero-Antúnez *et al.*, 2020; Zapata-Solvas *et al.*, 2012).

Recently discovered graphene consists of single layer of graphite with hexagonal lattice made of carbon atoms (single layer of atoms arranged in a two-dimensional honeycomb lattice). Physical, electrical, and thermal properties of graphene are exceptionally good and production of graphene is a simple and relatively low cost process (Novoselov, 2004; Geim and Novoselov, 2007).

Addition of CNTs and graphene exhibits completely different distribution of particles within ceramic matrix, thus indicating different final properties of the composite. CNTs tend to aggregate, while graphene is uniformly distributed throughout the matrix (Tapasztó *et al.*, 2011; Shen *et al.*, 2019). Grain refinement of the Si_3N_4 matrix was noticed with addition of graphene (Ramírez *et al.*, 2013). Combination of SiC nanoparticles with graphene as fillers for Si_3N_4 matrix has been studied for tribological applications (Llorente *et al.*, 2020).

Composites with carbon as a matrix material have showed great commercial success, especially those with carbon fiber as reinforcement (C_f/C composites). Excellent properties can be obtained by combination of carbon matrix and carbon fiber as reinforcement (C_f/C) that results in exquisite toughness. They have found significant applications in aerospace (rocket nozzles, thermal protection components in a spacecraft) and automotive industries (brake components material) (Chawla, 2019; Morrell, 2000). Carbon-based composites are also extensively used in manufacturing of high-temperature equipment in metallurgy and chemical industry, power and energy systems, friction systems and other (Trefilov, 1995). With all exquisite properties, carbon has an issue with oxidation at elevated temperatures, above 400°C (in air) and above 700°C (in steam), thus needing anti-oxidation protection (Chawla, 2019; Morrell, 2000). C/C composites exhibit low density, light weight, high strength and temperature resistance, good oxidation resistance (up to 400–500°C), good fatigue and creep resistance, does not have time-dependent degradation, and have very good compatibility with polymers, ceramics, as well as biological systems (Chawla, 2019; Morrell, 2000). C/C composites have been investigated to determine the relationship between the volume ratios of constituents, reinforcement distribution and orientation, and amount of porosity as composite properties on one side and their influences on final properties of the composite (Chawla, 2019). It was shown that small size of the matrix texture exhibited better interlaminar shear strength, whereas larger texture showed weaker matrix/fiber bonding with pseudo-plastic damage behavior (Blanco *et al.*, 2003).

Carbon can be combined in hybrid composites like C/C-ZrC-SiC with continuous ZrC-SiC ceramic matrix (Xie *et al.*, 2013) or C/C-SiC composites, where protective SiC layer was formed on the surface of carbon fibers (Yang *et al.*, 2020). C/C composites can be modified with ceramic fillers, like SiC nanopowder, to serve as high-temperature composites (Mikociak *et al.*, 2018). Different fillers have been studied aiming to realize fatigue strengthening of C/C composites. CNT-C/C composites showed better fiber-matrix interface and SiCNW-C/C composites exhibited strengthened matrix (Shen *et al.*, 2019). They showed that strength enhancement in these composites was achieved due to the shielding of main crack tip and its deflection, with occurrence of subcritical cracks that are closely related to the matrix anisotropy.

Even though their development is mainly focused on other fields, carbon-based composites are important for biomedical sector, as well. One of the carbon forms that is used as biomaterial is the low-temperature isotropic form, or pyrolytic carbon form (LTI carbon), with structure similar to graphite. It is biocompatible and thromboresistant (resistant to thrombosis - blood clotting) and have good strength and wear resistance, what makes it suitable material for implants that comes into contact with blood, such as heart valves and small orthopedic joints (fingers and spinal inserts). Thin coating of thromboresistant material on these implants will reduce the risk of thrombosis. Pyrolytic carbon can be also made in a form of fiber.

Composites with carbon nanotubes (CNTs) have been widely investigated for different applications (Nie *et al.*, 2020; Koltsova *et al.*, 2020; DeVries and Subhash, 2019; Belyakov, 2019). Carbon nanotubes are nanostructures with extremely high Young's modulus and mechanical strength and high electrical and thermal conductivity. Due to their small diameter (nano-scale), tubular geometry and high anisotropy, even small amount of CNTs in metal or ceramic matrix provides high performance composites with improved mechanical and physical properties (Jiang *et al.*, 2019; Tjong, 2009; Cho *et al.*, 2009). They show high resilience, and can sustain large strain without brittle fracture. CNTs can fracture during axial tensile deformation only at very high strains, above 30%. CNTs can be bent repeatedly under large angles, without failure (Tjong, 2009). Addition of CNTs into ceramic matrix directly significantly improves composite toughness, by all possible reinforcement mechanism: crack deflection, crack bridging and CNT pull-out (Xia *et al.*, 2004). Ceramic composites with CNTs are excellent for wear-resistant coatings.

Some authors found that CNTs have uncommonly high thermal conductivity in comparison to graphite and diamond. CNTs have exceptionally good electrical properties within a broad range, what depends on its dimensions and structure. Accordingly, CNTs have found wide applications in electrodes for supercapacitors, in catalysis, emission, and other similar fields (Jiang *et al.*, 2019; Tjong, 2009). CNTs have excellent electrical and thermal properties and are studied also from aspects of multifunctional properties that they might provide to CMCs (Cho *et al.*, 2009). Ceramics are widely known as insulating materials, but when conducting material is added, their electrical conductivity varies depending of volume ratios of both matrix and reinforcements. Addition of CNTs to ceramic transforms it from insulator to conductor, but with rather modest improvement (Tjong, 2009). CNTs have been added to electrical insulating ceramic, in order to tailor its electrical conductivity (Rul *et al.*, 2004).

Carbon nanotubes can be used as reinforcement material with various matrices. CNT-metal nanocomposites offer great combination of strength, stiffness and wear resistance compared to monolithic alloys. Also, implementation CNTs into metal matrices does not impair fracture toughness of metals. These types of composites found their application in transportation, chemical and electronic industries, especially in thermal management applications due to CNTs exquisite thermal conductivity (Tjong, 2009). Addition of CNTs to hybrid metal-based composites with Al matrix (AMCs) produces aluminum carbide (Al_4C_3) at CNT/matrix interface, thus changing micromechanical behavior and significantly improves effective mechanical properties of the composite (Nie *et al.*, 2020). MWCNTs-reinforced alumina composite coating on the steel have decreased corrosion rate of the boiler steel (at 900°C), by 30–70%, thus indicating that this type of CMCs can be successfully used in hot corrosive environments (Goyal *et al.*, 2020).

Rubber is one of the widely used materials across all industries, from simple sealing to tires in automotive and aircraft industries (Aliofkhazraei, 2019). Addition of CNT fillers in rubber matrices significantly improves mechanical properties. Since CNTs possess high aspect ratio and surface area, as well as high mechanical properties, they represent ideal reinforcements for these types of matrices, improving mechanical, thermal and electrical properties of rubber. In terms of mechanical properties, tensile strength increases with the addition of CNTs, in cases of both natural and synthetic rubbers. However, the strain at failure decreases, and Young modulus increases almost by 8 times for the 10 wt% of CNT, according to some research (Aliofkhazraei, 2019). Also, the tear strength increases with the increase of CNT content, as well as matrix hardness. These types of composites have found their applications according to their increased mechanical properties, like O-ring sealing in oil containers. On the other hand, increase of electrical conductivity makes these elastomers suitable for sensor and semiconductor applications.

Graphene is one of the novel reinforcement materials that have a potential to significantly improve properties of CMCs, especially electrical and thermal conductivity. However, incorporation of graphene nanoparticles (usually platelets) in ceramic matrix is still a challenging topic. Graphene reinforced alumina (GNPs- Al_2O_3), graphene-SiC composites, Si_3N_4 ceramic with dispersed multilayered graphene, graphene-ZrO₂ CMCs, GNPs-AlN, graphene-SrTiO₃ have been fabricated and extensively studied, in order to understand governing physical and chemical mechanisms, as well as mechanical and other properties (Zhou *et al.*, 2020a; Huang and Wan, 2020; Nieto *et al.*, 2017; Porwal *et al.*, 2013). Potential application areas of these novel CMCs are versatile: electromagnetic interference shielding, high impact resistance components (ballistic), damage sensors, energy storage systems (Huang and Wan, 2020), as well as in biomedical applications (Liu *et al.*, 2015; Liu *et al.*, 2013, 2012).

Graphene platelet-reinforced alumina ceramic composites (Liu *et al.*, 2013), and graphene platelet/zirconia-toughened alumina (GPL/ZTA) (Liu *et al.*, 2012) were evaluated as structural materials. In ZTA composites, addition of GPLAs increased fracture toughness by 40%. Addition of graphene nanoplatelets (GNPs) in SiC matrix produced and increase in fracture toughness by 160%, increase of strength by 60% (Belmonte *et al.*, 2016). In alumina matrix, the addition of graphene produced hardness

increase by 7%, grain size refinement by 46% and fracture toughness increase by 72% (Ahmad *et al.*, 2015; Shah *et al.*, 2020). Processing routes of graphene are very important also for metal matrix composites, like Cu-based composites (Zhang *et al.*, 2020c).

Recent Advances and Future Research

There is a large scope of literature with different matrix/reinforcement combinations in CMCs, including hybrid composites and their processing routes, like SiC nanowires in hybrid CMCs (Liu *et al.*, 2020a). Versatile applications are studied, as well as new characterization methods, especially those related to determination of composite properties during functioning and at micro and nano scales. New biodegradable composites are investigated and their behavior, like MgO/HA ceramic nano-composites for bone grafts (Khalili *et al.*, 2021). Design of composites is strongly influenced by the possibilities to mimic natural structures, what have been enabled by experimental characterization techniques at nano and micro scales. Development of CMCs also included some of these methods, like the design of nacre-like aluminas (Bouville, 2020).

Development of new techniques and methods in characterization of CMCs is very important, because it is the necessary support in new composite development. New approaches and methodologies appear, like method of symbolic-graphic combination for identification of interface shear stress of CMCs, under fatigue loading (Han *et al.*, 2021). Damage monitoring can reveal underlining phenomena in composite degradation. Goulmy *et al.* (2021) proposed crack density-based electromechanical model for damage evolution monitoring in CMCs. For one of the mostly used CMCs, SiC_f/SiC ceramic, tensile creep behavior is still under study (Almansour and Morscher, 2020), as well as the influence of physical and chemical properties on fiber cracks (Mazerat and Pailler, 2021); residual stresses and their relationship with mechanical behavior (Chen *et al.*, 2020a) and effect of braiding angle on fracture behavior (Chen *et al.*, 2020b). In general, creep and fracture of CMCs is subject of research also at normal temperatures (Li, 2021). Real-time imaging is challenging under high temperatures above 1600°C (Bale *et al.*, 2013).

Metal reinforcement of ceramic matrix is challenging, due to adhesion issues and high temperatures in ceramic processing. Increase of metallic phase usually decreases the densification temperature, like in Al₂O₃-Cu-Mo system, with Al₂O₃ matrix (Zygmuntowicz *et al.*, 2020). However, in this case matrix surface still exhibited brittle fracture. New approaches in fabrication of CMCs include microwaves in material processing (Mishra and Sharma, 2016) and laminated structures (Dermeik and Travitzky, 2020). Additive manufacturing has offered easier and less costly fabrication methods (Zhou *et al.*, 2020b).

Development of wear resistant and self-lubricating materials under high temperatures is very important for different applications (Greil, 2020), including specific tribo-materials (Hernandez *et al.*, 2020). Si₃N₄ ceramics with addition of SiC nanoparticles and graphene have been studied in this regards (Llorente *et al.*, 2020). Addition of GNPs in hybrid WC-Al₂O₃ ceramic composite produced grain refinement, and increase of hardness and fracture toughness, with simultaneous reduction of friction coefficient (by almost 50%) and wear rate (Zhang *et al.*, 2020d). This indicates that these composites have high potential for tribological applications. Porous alumina matrix reinforced with MoS₂ particles exhibit hollow fullerene-like structure and excellent wear behavior (Salam *et al.*, 2021). Another composite with excellent tribological properties was produced by using ceramic waste SiC particles in aluminum matrix composites, for application in high-performance brake disks (Zheng *et al.*, 2020).

Important research is related to electromagnetic shielding (Yin *et al.*, 2017) and sensors through development of metacomposites with negative permittivity (TiN/Al₂O₃ ceramic composites) (Hou *et al.*, 2021) or neutron shielding composites (B₄C reinforced Al₂O₃-ZrO₂ ceramic with Gd₂O₃-CA6 layer) (Hei *et al.*, 2020). Microwave absorbing properties for aerospace applications are also investigated, such as Al₂O₃/SiCN composite (Liu *et al.*, 2020b) or Ni-loaded ceramic composites (Zhu *et al.*, 2021). Combination of SiC nanowires and graphene in ceramic matrix has been studied for applications related to electromagnetic wave absorption (Jia *et al.*, 2018; Han *et al.*, 2016). Particulate graphene reinforcement can form electrically functional network in ceramic matrix and this phenomena needs further investigations (conducting and dielectric ceramic matrices) (Miranzo *et al.*, 2018).

Protective materials are very important today, such as environmental barrier coatings for hostile environments like gas turbines, in order to reduce CO₂ emissions (Tejero-Martin *et al.*, 2021; Lee *et al.*, 2021). Also, possibilities to utilize vast quantities of sub-products like carbon black (C_{black}) in composites such as silicon oxycarbide (SiOC)-based ceramics (de Almeida Silva *et al.*, 2020) or to produce sustainable composites, reinforced with natural fibers, like basalt fibers (Fiore *et al.*, 2015), are important and in accordance with environmental concerns. Some latest research showed that SiC nanowires grown on carbon fibers in CF/ZrC composites, can offer new properties of CMCs for thermal protection components (Yan *et al.*, 2018).

Energy applications of CMCs are important, especially considering new energy harvesting systems, piezo-devices (like ultrasound sensors), flexible electronics, advanced precise sensors and electronics (Bumgardner *et al.*, 2021; Wang *et al.*, 2015; Wang *et al.*, 2011). New developments in piezoelectric (PZT) ceramic composites promise controllable and active highly-precise sensors, energy harvesting systems and new material classes of ferroelectrics (FE). PZT ceramic-crystal composites are under study to determine their electro-physical properties and complex relationships between material properties (physical and chemical properties, constituents, volume fractions, porosity, microstructure, etc.) and elastic, dielectric, and piezoelectric parameters of PZT active composites. Recent research has been related to development and characterization of CMCs like PbTi_{0.45}Zr_{0.53}(W_{1/2}Cd_{1/2})_{0.02}O₃ (PZT piezoceramic matrix with crystalline microparticles of LiNbO₃) (Lugovaya *et al.*, 2018); Pb[(Mn_xNb_{1-x})_{1/2}(Mn_xSb_{1-x})_{1/2}]_y(Zr_{0.5}Ti_{0.5})_{1-y}O₃ (PMN-PMS-PZT) ceramics with dispersed phase of thermally conductive AlN (Wang *et al.*, 2018); (hBN) nanosheets dispersed in Pb[(Mn_{1/3}Nb_{2/3})_{1/2}(Mn_{1/3}Sb_{2/3})_{1/2}]_{0.04}(Zr_{0.95}Ti_{0.05})_{0.96}O₃ (PMN-PMSPZT) ceramic matrix (Wang *et al.*, 2019); 3D interconnected piezoelectric microfoams for energy harvesting (Zhang *et al.*, 2018); PZT-based materials with aligned porosity (Zhang *et al.*, 2019); lead-free 0.50[Ba(Zr_{0.2}Ti_{0.8})O₃]_{0.50}(Ba_{0.7}Ca_{0.3})TiO₃ (BZT-BCT) ferroelectric powder dispersed in polyvinylidene fluoride (PVDF) matrix, for flexible electronics

(Riquelme and Ramam, 2019). Electro-physical properties of these composites strongly depend on the structural and mechanical properties of piezoceramic matrix and dispersed crystalline phase, as well as internal microporosity (and composite porosity up to 60%). It has been determined that microporosity of ceramic matrix has essential effect, beside the matrix and filler properties, on elastic, dielectric, and piezoelectric parameters of PZT CMCs (Lugovaya *et al.*, 2018). These pyroelectric CMCs can be used for harvesting of waste heat in energy harvesting devices (Wang *et al.*, 2018, 2019). Flexible electronics have become the center of research attention recently, aiming at development of versatile electronic wearables, as biomedical sensors (Riquelme and Ramam, 2019). Interconnected network formed by dispersed crystal phase in highly porous ceramic matrix (micro-foam) enables continuous pathway for load transfer (Zhang *et al.*, 2018; Zhang *et al.*, 2019). Such ceramic foam is shown to provide excellent pyroelectric properties that can be used in high-performance energy harvesting (both thermal and mechanical energy) and for self-powered micromechanical devices. However, inter-relationships between the composition, structure and properties of those composites are very complex and still need to be studied, including dielectric, ferroelectric, and piezoelectric analyses.

New research directions include functional nanocarbon hybrids. In nanocarbon hybrids, nanocarbons (fullerenes, CNTs, graphene) have close contact with second active component, focusing on composite performance such as photovoltaics, catalysis, supercapacitors, sensors (Shearer *et al.*, 2014). Novel phosphor-glass composites for high-power white light-emitting diodes were fabricated by pressureless sintering (Zhang *et al.*, 2020b).

Another emerging group of CMCs is ultra-high temperature ceramic matrix composites (UHTCMCs), with ZrB_2 -SiC matrix, for rocket and hypersonic vehicle components (Binner *et al.*, 2020; Mungiguerra *et al.*, 2020; Adibpur *et al.*, 2020; Padture, 2016). Coatings on carbon fibers still represent challenging topic, and processing routes are investigated. New research results revealed that it can provide excellent fracture toughness, such as in the case of $\text{C}_{\text{F-PyC}}/\text{ZrB}_2$ -SiC composite that exhibited non-brittle fracture (Zhang *et al.*, 2020a).

Conclusions

Ceramic matrix composites (CMCs) have been developed and applied mainly for components working under high temperatures, and harsh corrosive environments, including ultra-high temperatures and extreme loading. Both oxide and non-oxide CMCs are developed primarily to increase the toughness of the ceramics. The main role of the reinforcements in ceramic matrix is to provide support to a very brittle ceramic matrix that lack toughness, in order to arrest crack development and prevent catastrophic failure. Well-designed bond between matrix and reinforcement should support load transfer, as well as crack deflection by debonding, pull out and fracture of the fibers. Aerospace applications still represents the most influential drive for the development of CMCs, like ultra-high temperature ceramic matrix composites (UHTCMCs), but other areas have also dedicated research attention to CMCs. Carbon fiber-reinforced silicon carbide (C/SiC) CMCs are among the most famous composites for high-temperature structural applications. Development of bioceramics, including glass ceramics, calcium phosphates and more recent bioactive ceramics and bioglasses (bioactive and bioresorbable), have significant impact on the development of biomedical devices. Hybrid composites and composites with nanostructured reinforcements, like carbon nanotubes (CNTs) and graphene, have opened diverse new areas of applications. New design of CMCs for smart materials, including electromagnetic shielding, energy harvesting systems and piezo-devices, will significantly contribute to the current trend of smart and wearable electronics.

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Processing Routes for Ceramic Matrix Composites (CMCs)

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Introduction

Ceramic matrix composites (CMCs) have gained significant attention because they can greatly improve the properties of pure ceramics and especially overcome lack of ceramic toughness. CMCs offer low weight, high strength, high temperature resistance and chemical inertness in hostile environments, due to which their development has been primarily associated with aerospace applications. Development of CMCs is mainly focused on their application as structural and thermostructural materials (Tressler, 2001). They are also widely applied in other areas where components work in hostile environments (e.g., heat engines, nuclear reactors, turbine blades, etc.). CMCs are used in transportation, including automotive, and rail industries, electronics, energy conversion and storage devices, biomedical devices and other fields.

Extensive research has been devoted to the concept of damage control and prevention in structural components, like in all responsible vehicle systems, such as brakes, shafts, shock absorbers, elements of the car/rail vehicle body (e.g., contact patch in railway coupling) and other extensively loaded elements. Harsh in-service conditions require specific material properties, such as strong wear and corrosion resistance, resistance to fatigue or impact cracking, resistance to thermal shocks, good mechanical properties within different temperature ranges, also with fluctuating temperatures, adequate aging properties, etc. Lightweight elements are needed for many reasons but very rarely light structures can satisfy the necessary properties in hostile environments. Lighter vehicles primarily mean less energy and fuel consumption and reduced CO₂ and NO_x emissions, with preserved vehicle power, as major requests nowadays. Added value of CMCs in automotive elements is the possibility to recycle them after use, since traditional brake surfaces usually contain environmentally harmful heavy metal particles. Research results strongly indicate that even the small amount of long fibers in ceramic matrix significantly increased toughness and crack resistance, including thermal shock resistance.

Ceramics in general have very low wear in contact with majority of other materials, even under high loads and significantly lower weight than metals, especially iron-based alloys and steels. It is ideal material from aspects of wear and corrosion resistance, but traditional ceramics have low crack resistance and they might even crack under the influence of small scratches (Zivic *et al.*, 2013), exhibiting brittle cracking, especially under impact loading. Ceramic materials are costly solution compared to standard materials. For example, steel or cast iron with nodular graphite is commonly used as low cost solution for automotive brakes, whereas ceramic-based materials can offer better properties, but with significantly higher cost. Current research area relates to full brake systems made of CMCs (both brake disks and pads), to provide lightweight, high friction, high corrosion and wear resistance also under elevated temperatures and high loading, including impact (Stenkamp and Schorn, 2014; Krenkel, 2002). CMCs can provide excellent thermo-mechanical properties, with low weight. Studies strongly indicated that their high cost can be influenced through the production costs in order to become more available material for automotive and rail elements (Langhof *et al.*, 2016).

Ceramic-based composites that are widely studied for applications in different areas, especially in transportation sector, are carbon fiber reinforced carbon composites (C/C). They have already been applied in race cars and aircrafts. However, there are still some issues with carbon-based composites, mainly due to low oxidation resistance and low friction coefficient of carbon fibers in humid environments and temperatures below 200°C. Different coatings have been studied on carbon fibers to improve their oxidation and thermo-mechanical properties. There is also large scope of research related to different combinations of composite constituents (particles, platelets, whiskers, fibers) also including hybrid composites, with combinations of reinforcements.

Application of CMCs is wide, but still not massive as in the case of polymer-based composites, mainly due to their high production costs. Fabrication of components made of CMCs is not easy, since the majority of processing involves high temperatures. Unlike other composite classes made of metal or polymer matrix, there are only several techniques and methods for producing ceramic matrix composites, and not even all of them are commercially feasible methods. Unlike metal or polymer matrices, ceramic matrix is dense and hard and the fabrication of CMCs commonly does not start with fabrication of matrix and later addition of reinforcing phases. In case of fiber reinforced CMCs, ceramic matrix is commonly derived from precursors which is positioned around the reinforcement phases. Additional approach is preparation of in situ CMCs, meaning that all composite phases are produced in situ, all at once. According to the literature, different methods can be used for the production of ceramic matrices: chemical vapor infiltration (CVI) (for carbides, nitride carbon, oxides, etc.); hot pressing (for glass matrices; oxides); sol – gel (for oxides); polymer precursor route (SiC, Si_xN_y, Si_xC_yN_z); liquid metal infiltration (SiC); prepreg curing and pyrolysis (SiC, Si₃N₄) (Rosso, 2006). There are three general groups of methods for fabrication of CMCs (Rayat *et al.*, 2017; Naslain and Pomeroy, 2016):

- (1) Powder dispersion (solid phase processes),
- (2) Liquid precursors (liquid phase processes) and,
- (3) Gaseous infiltration (gas phase processes).

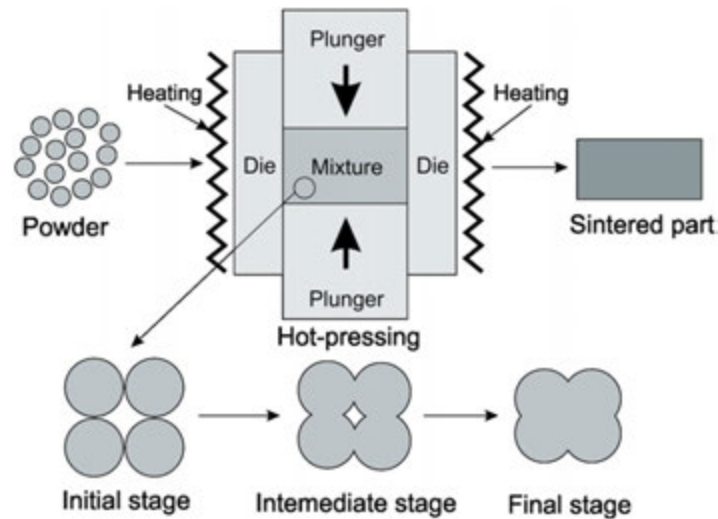


Fig. 1 Schematic representation of the sintering process.

This article shortly reviews the main conventional production and processing methods and provides references for new research directions.

Processing of Ceramic Matrix Composites (CMCs)

Solid Phase Processes

Solid phase processes accounts for around 50% of all technologies that are used for fabrication of CMCs (Rayat *et al.*, 2017). However, these are mainly limited to short fiber reinforcements (Naslain and Pomeroy, 2016), because with long fibers, composites are prone to cracking when fabricated by powder processing. Common technology is sintering (shown in Fig. 1), where thermal treatment of powders produces solid structure through mass transfer at atomic scale (German, 2010; Moya *et al.*, 2003). Sintering is used for production of wide variety of components and materials, like oxide reinforced superalloys for high temperature motors, dental amalgams, biomedical implants, elements of cutting tools, and many other. Resulting solid material always exhibit certain level of microporosity, even with high densification. In order to improve densification during sintering (Matovic *et al.*, 2016) and prevent crack development, it is necessary to introduce weak phases like graphite in SiC (Clegg *et al.*, 1990). Also, not all ceramic materials exhibit necessary sintering activity to enable full sintering. Traditional powder processing (powder metallurgy and slip casting) also has a limitation related to complexity of component geometry, thus only simple geometries can be produced. High densification properties are an advantage, and there are different methods to improve it, like vacuum processing (Zivic *et al.*, 2012). Uniform distribution of the reinforcement phase in the matrix can be difficult to achieve. There is a risk of damaging the reinforcement during the compaction process. Novel additive manufacturing (AM) technologies have enabled fabrication of complex shapes and structures, as well as hybrid composites (Lakhdar *et al.*, 2021). For example, biomedical ceramic, like standard PMMA, is widely used as medical adhesive and in some cases as bone graft. However, producing shapes and structures that resembles geometry of the living organ is difficult, even with additive technologies. Some recent attempts to use AM for fabrication of biomedical implants proved as successful in fabrication of custom made sternum bone made of PMMA, with incorporated anchors for fixing it within the sternum cage (Stojkovic *et al.*, 2010).

In general, powder processing starts with homogenous powder mixtures of matrix and reinforcement materials, together with binding agent, which is usually prepared by ball milling. It can be in dry or wet state. Afterwards, the mixture is put in a die and sintered (uniaxial hot pressing or isostatic cold pressing). Dry pressing is used for the production of Si_3N_4 matrix composites and some alumina matrix composites. Powder processing of CMCs often requires both very high temperature and pressure, as one disadvantage of this technology (Rayat *et al.*, 2017). Also, short fibers usually result in lower mechanical properties than continuous fiber reinforced composites. One approach to improvement of properties is the development of hybrid CMC composites, with combinations of short fibers and particulates as reinforcement phases (Kelly and Zweben, 2000).

Slurry processing

When making CMCs from powders and slurries it is important to achieve a homogenous mixture and good packing efficiency of reinforcing particles. That can be especially hard in powder mixtures where toughening particles are in the form of whiskers, which tend to get more easily damaged than other forms of reinforcements. Using aqueous solutions helps with the mixture homogeneity. Accordingly, wet slurry processing is sometimes preferred to powder processing. When using aqueous slurries pH balance is of great importance for the proper dispersion of the constituents.

An example of a slurry-based process is the production of mullite-based composites with oriented SiC whiskers by tape casting technology. Tape casting refers to the process of producing thin CMC sheets with adequately oriented whiskers, then stacking them and keeping the stack at certain pressures and temperatures for some time, which is referred to as lamination. During the process of lamination, the binder is removed (usually burned out due to high temperatures).

A similar process can be done with aqueous slurry of glass particles, through which SiC fibers are passed. Such glass-ceramic composite usually requires additional heat treatment, due to insufficient crystallization during hot-pressing (Carter and Norton, 2013).

Hot pressing

Hot pressing is a technology commonly used to produce low-porosity composites containing whiskers, suitable for glass and ceramic materials. Whiskers can be easily damaged and difficult to disperse in a homogenous manner, therefore the process must be carefully controlled. Hot pressing is realised under high pressure, high temperature and low strain rate. Dies for hot pressing are exposed to high temperatures (Fig. 1), so they must be produced from expensive heat-resistant materials. This technology can enable only simple-shaped final products, such as cylinders, flat plates, blocks, etc. (Carter and Norton, 2013).

Hot pressing is used to manufacture alumina-based composites with carbon nanotubes (CNTs) and SiC reinforcements. Alumina-based composites with various reinforcements such as CVD-CNT, single-walled carbon nanotubes (SWCNTs), multi-wall carbon nanotubes (MWCNTs) and TiC can be made by spark plasma sintering, while microwave sintering can be employed to make alumina-zirconia and alumina-titania composites, along other traditional methods (conventional sintering, cold pressing). Microwave sintering is used for ZrB₂ matrix and SiC matrix composites as well (Rayat *et al.*, 2017).

Novel sintering techniques

Microwave (MW) sintering is an effective sintering technique with a reduced sintering time and high product density suitable for CMCs and cermets. Materials that are sintered by using microwaves have good mechanical properties and fine microstructures. MW sintering has been successfully used for Al-based composites and nanocomposites. Microwaves can provide rapid and uniform heating, due to being directly absorbed into the material and rapidly converted into heat. They are also considered environmentally friendly because of their green energy source and the absence of toxic gases (Tiwari *et al.*, 2016; Gerdes and Whxert-Porada, 1994; Khan *et al.*, 2020; Guo *et al.*, 2019).

Flash sintering process combines electricity with high temperatures in the furnace. Material rapidly densifies and the sintering process is very quick. Flash sintering requires a much lower temperature furnace than conventional sintering because the Joule effect electrically heats the material, concentrating the heat in the ceramic placed in an electric field (Biesuz *et al.*, 2020).

Spark plasma sintering (SPS) process combines electricity with external uniaxial pressure. It is similar to flash sintering in the sense that the Joule effect provides heating, but most of the heat is generated in die and punches, unlike in flash sintering where heat was generated internally (within ceramic). Spark plasma sintering is versatile and can be used for polymers, as well as metals and ceramics, but it is also a complex and expensive technique. Another drawback is that it can only produce simple shapes, due to the uniaxial rigid press tool system (Biesuz *et al.*, 2020; Guo *et al.*, 2019).

Flash cold sintering combines electricity and water, resulting in the electrolysis of water at room temperature. Some external pressure is needed, as well. This process can produce dense ceramics faster than cold sintering and with no external heating (Biesuz *et al.*, 2020; Kermani *et al.*, 2020).

Cold sintering process (CSP) and Cold sintering (CS) refer to different techniques, even though they sound similar. CS is used for ductile materials such as metals, to sinter them at low temperatures (around room temperatures) under dry conditions, while CSP refers to the ceramic powder sintering technique that employs a transport liquid phase (usually water) and uniaxial pressure, with temperatures below 350°C. Good solubility of the ceramic powder in the liquid is desirable. Uniaxial pressure and capillary forces drive the densification process. The system is not hermetically sealed and controlled water evaporation is the key point. Without evaporation of the liquid, proper densification cannot happen, meaning that the most of the liquid phase need to escape the pores. Only simple shapes are possible due to uniaxial pressure (Biesuz *et al.*, 2020; Guo *et al.*, 2019).

Liquid Phase Processes

Liquid phase processes use liquid precursor to infiltrate reinforcements. Liquid precursor is usually polymer or solution that solidifies at elevated temperature (curing or gelling), decomposes and form ceramic matrix around reinforcements. Sol-gel, polymer infiltration pyrolysis (PIP), reactive melt infiltration (RMI), slurry impregnation and hot pressing (SIHP), are commonly used methods. The advantage of liquid phase processes is the possibility to form complex geometries. Traditional chemical processing, sol-gel, usually involves several phases: deposition of chemical solution on reinforcements, different chemical reactions depending on the reinforcement material, gelation, aging, drying, densification, and crystallization. In PIP processes, commonly used precursors are thermosetting polymers. The fibers are surrounded by liquid precursor, cured, pyrolyzed and heat treated. However, these methods can be inefficient and costly, in terms of repetition of infiltration and decomposition steps until the desired CMC is achieved. RMI process is fast and can be used with materials that have relatively low melting point (e.g., Al, around 650°C, or silicon, around 1400°C). Aluminum can form alumina matrix through oxidation process. Silicon can form SiC matrix by chemical reaction with carbon-based preform fibers. Resulting CMCs always have some level of internal porosity, because the process stops when the pores become blocked, thus forming closed pores inside the composite. Low production rate

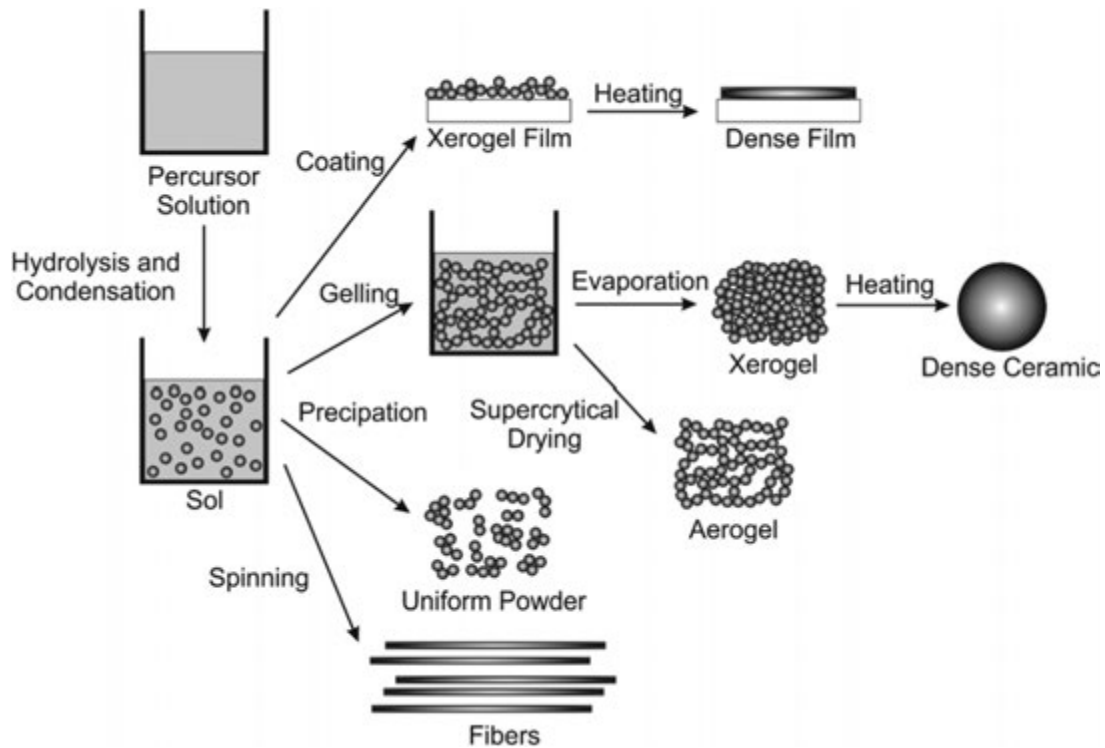


Fig. 2 Schematic representation of sol – gel processing in fabrication of ceramic matrix composites, fibers, and thin films.

and cracks in the matrix during cooling are some of the recognized issues. Sol-gel and PIP processes use lower densification temperatures and have good control over the matrix compositions while being low cost technologies.

Sol-gel

Sol-gel process is a chemical method of material synthesis. It is one of the mostly used techniques because of its efficiency. Significant advantage of the sol-gel method is that it can provide stable materials, as well as surfaces. Material properties can be rather precisely tailored by the chemical processes. Sol-gel process can have several phases and different chemical reactions, as previously stated, but in general, it essentially involves: (1) precursor hydrolysis and (2) their polycondensation (Yilmaz and Soylak, 2020). Schematic representation of sol – gel processing in fabrication of ceramic matrix composites, fibers, and thin films is given in Fig. 2.

Sol-gel processing needs oxide source (usually metal alkoxides and acetylacetonates), hydrolysis (usually by water), solvent (alcohol), and catalyst agent. Process is usually developing at room temperature. Solid phase that grows out of solution consists of uniformly dispersed fine particles, if the clean conditions are maintained. Particles are further bonded in a gel form that still contains water and solvents. Generally, different shapes are formed during the sol to gel transformation. Evaporation of water and solvent produces a dried gel. Gel heating up to a several hundred degrees produces thick oxide materials as final products (Sakka, 2013). Different functional materials are produced by sol-gel, such as photocatalysts, ferroelectrics and many more. It is used for preparation of non-silicic oxides, including TiO_2 , ZrO_2 , Al_2O_3 , ZnO , WO_3 , Nb_2O_5 , rare earth oxides, etc. (Sakka, 2013).

Reactive melt infiltration (RMI)

In reactive melt infiltration (RMI) ceramic matrix is formed around the fiber prepreg, by metal oxidation process. As previously stated, this process requires rather low melting point of the starting material. In general, two methods are applied: liquid silicon infiltration (LSI) and direct melt oxidation (DIMOX). DIMOX is commonly used for production of Al_2O_3 matrix, from molten aluminum (Al). LSI used for fabrication of SiC matrix from silicon (Si) melt that is infiltrated to the carbon (C) preform. Composites produced by RMI process usually have high thermal and electrical conductivity. Final composite may have some residual metal beside the matrix itself (Al_2O_3 matrix with residual Al; SiC matrix and some residual Si). The process is realised under high temperatures that cause chemical reactions between the molten matrix and the dispersed fibers (porous preform). The liquid metal infiltrates the porous preform and forms the matrix throughout the structure. Some residual porosity is present in the final composite, but it is usually low. Metal flow through the porous preform can be spontaneous due to capillary forces (Kopeliovich, 2018; Wali and Yang, 2012), or it can be driven by external pressure (vacuum, centrifugal force, electromagnetic field, etc.), in case of poor wettability of ceramic. This technology has been combined with other methods (e.g. slurry infiltration) to produce other ceramic composites, like carbon fiber reinforced ZrB_2 composites (Vinci et al., 2020).

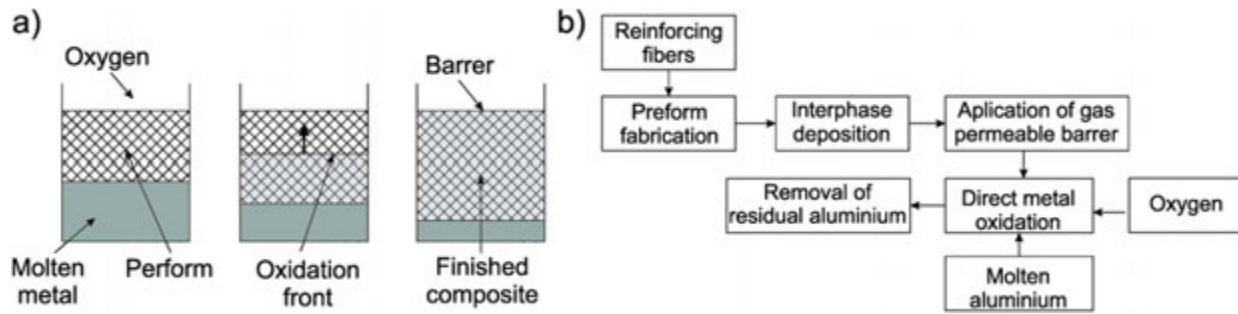


Fig. 3 Schematic representation of direct melt oxidation (DIMOX).

Interactions between liquid and solid that determine the wetting have been long studied, including composite structures. Wettability is defined by the relationship (balance) between adhesive and cohesive forces. Different interactions of thermodynamic nature that occur on solid-liquid, solid-vapor, liquid-vapor interfaces altogether influence the resulting wettability, because it depends on both the solid surface state and environment (Mileiko, 1997; Park and Seo, 2014). However, theoretical understanding of the wettability is still at simple ideal solutions (capillary model) that cannot be directly correlated to the real process. Simulation of the RMI process is complex (Grujicic et al., 2015) and definitive governing mechanisms are still unknown. Some research indicates that the main influential factor to slow the metal infiltration is phenomenon of pinning (Sergi et al., 2016). Some recent research elaborates that gas phase reactions are the governing factor in RMI process, instead of capillary effect (Hofbauer et al., 2019, 2020). In reality, infiltration process at high temperatures is strongly influenced by many aspects, such as surface roughness, chemical homogeneity, and morphology of pores, partial solidification, and formation of reaction layers that can close pores and stop formation of the matrix. Chemical reactions are time-dependent and can provoke different additional processes that can further change solid-liquid interfaces and capillary forces. Also, in case of particulate reinforcements, fluid shear can redistribute the composite structure.

Direct melt oxidation (DIMOX) has been used for alumina-based composites for years. A schematic representation of the process is shown in Fig. 3. In general, there are four stages: (1) fiber pretreatment, (2) formation of fiber preform, (3) green fiber preform, and (4) infiltration process. Molten aluminum is brought into contact with a preform (that can contain fibers and/or particles), within the environment that contain oxidizing agent (oxygen). It is necessary to provide the following: melt wettability of dispersed phase and chemical inertness of the reinforcement to an oxidizing agent. Thin ceramic film is formed on the dispersed phase by oxidation of the liquid phase. Rate of oxidation is in direct correlation with melt advance. Growth of oxide can continue also after the whole preform was infiltrated, what can be prevented by gas permeable barrier (Kopelovich, 2018). Possibilities to use different reinforcements (particulates) are studied (Santhosh Kumar et al., 2012), and also effects of alloying elements additions (Zn, Mg) to improve the process (Pourbakhshi et al., 2020). Also, preforms with porous fibers can enable efficient production of hybrid composites (Jiang et al., 2021).

Liquid silicon infiltration (LSI) is used for production of C/SiC composites that have the widest applications (brake and sliding elements in automotive and railway industry; different high-temperature elements in aerospace industry, like gas turbines, rocket engines, shields, flaps; structural parts in satellites; components in optical devices; components in microelectronics; heat exchangers in nuclear power plants; elements of ballistic systems. Accordingly, it has been important subject of current research, aimed at different applications, like thermal energy storage systems (Stahl et al., 2020)), rocket propulsion systems (Olufsen and Ørbekk, 2017), space applications and advanced friction systems (Krenkel and Berndt, 2005) and different aspects in two-phase or hybrid composites: thermal residual stresses that induce matrix damage (Stahl et al., 2020), improvement of oxidation resistance of hybrid Cf/C-SiC composites (Mubina et al., 2020), development of short-fiber-reinforced C/C-SiC composites (Nier et al., 2020), production of superhard SiC bonded diamond materials (Matthey et al., 2020), effects of different carbon precursors (Roder et al., 2014).

Gas Phase Processes

Gas phase processes use reactive gas mixture that is infiltrated into the pore network of the preform (fiber bundles) and provokes chemical reaction with reinforcements and environment which produces ceramic matrix with firmly embedded fibers. These processes are commonly realised under high temperatures. Standard methods are reaction bonding, chemical vapor deposition (CVD), and chemical vapor infiltration (CVI). As in previous liquid phase processes, there is always some remaining closed pores within the final structure, without the completely full densification of the matrix. Gaseous infiltration is slow process, because the fast processing would block the gas penetration by closing the external zones, while the internal ones would stay with extensive level of porosity. Reaction bonding can rapidly produce near-net shape products, but it is limited to simple shapes and characterized by high porosity and high cost. In CVI process, fiber coating (interphase) is realised prior to the matrix infiltration, in order to control the chemical reactions and fiber/matrix bonding, as well as final mechanical properties of the composite. There are several types of CVI processes, as shown later in this article. Gas phase processes have higher densification rate, lower time of

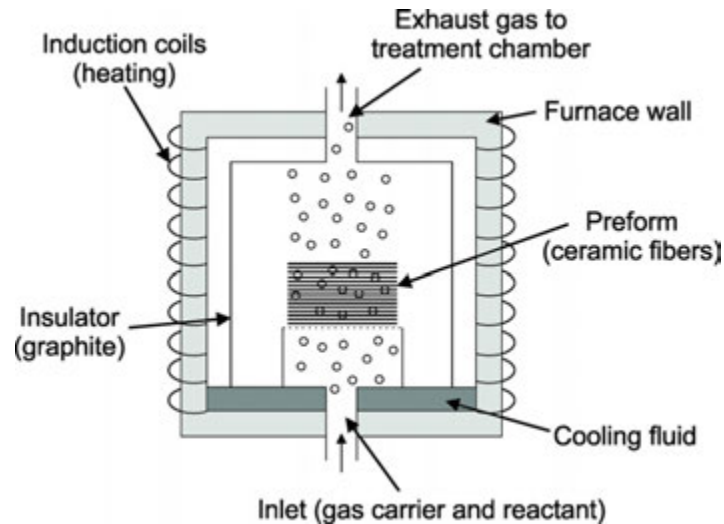


Fig. 4 General concept of Chemical Vapor Infiltration (CVI) process.

processing and lower temperatures in comparison with previous methods. Final composites have better resistance properties (Rayat *et al.*, 2017). CVI is characterized by a high deposition rate, enhanced mechanical properties of the finished products and can be used with many materials, but it is also expensive, have hazardous by-products and, due to difference in thermal expansion coefficients, can produce residual stresses. CVI is a flexible method for producing complex shapes, but the disadvantages are long processing time and low production rate, as well as a high cost.

Chemical vapor infiltration (CVI)

Chemical Vapor Infiltration (CVI) is a common method for processing of SiC/SiC composites with continuous fibers. SiC matrix is formed from methyltrichlorosilane (MTS) precursor, which is supplied to the preform by the carrier gas (usually hydrogen, argon or helium). Gaseous phase infiltrate porous preform (by diffusion or external pressure) and deposit the ceramic matrix upon the surface of the fibers. CVI is also widely accepted processing techniques for C/C composites (Chawla, 2019; Leuchs, 2011). CVI technology uses the same concept as Chemical Vapor Deposition (CVD) where the reactant gas acts upon the surface of the substrate (Prelas *et al.*, 1997; Choy, 2003).

From the preform, the gaseous hydrogen chloride (HCl) is removed by the diffusion or forced out by the carrier stream. Carbon matrix is formed from a methane precursor (CH_4) (Carter and Norton, 2013). Deposition of ceramic matrix is realised until the diffusing vapor can reach the reaction surface. The porosity of the material is decreasing because it is filled with the formed solid ceramic. Disadvantage of the CVI process is its slowing as the vapor fills out the pores and closes the open path. When all the preform pores are closed densification of the matrix is stopped. Pores and voids that cannot be accessed because they are closed by the deposited material, are left within the composite structure and form internal residual porosity. The final residual porosity of the ceramic composites fabricated by CVI method may reach 10%–15% (Carter and Norton, 2013). General concept of the CVI process is shown in Fig. 4.

Chemical Vapor Infiltration process is classified into five types, as shown in Fig. 5., depending on the transfer method of gaseous precursors, as follows (Choy, 2003):

- (1) isothermal/isobaric (I-CVI),
- (2) thermal gradient (TG-CVI),
- (3) isothermal-forced flow (IF-CVI),
- (4) thermal gradient-forced flow (F-CVI) and
- (5) pulsed flow.

Isothermal/isobaric (I-CVI) is the simplest, and the most commonly used type of CVI process. The reactant gas is supplied to the preform at a uniform pressure, with no pressure variations. Also, there is no variation of the temperature. It is a slow process due to the low diffusion rate.

Thermal gradient (TG-CVI) process uses the temperature gradient. Within the chamber, surfaces are at different temperatures, thus forming cooler and hotter zones that promote diffusion of the gas. Matrix formation is usually concentrated within the hot zone since the reactions are more rapid there. This process fabricates composites with lower porosity level.

Isothermal-forced flow (IF-CVI) process uses the pressure gradient, while the preform is uniformly heated. Increased pressure increases the deposition rate. It is useful for fabrication of thin walled structures (e.g., filters).

Thermal gradient-forced flow (F-CVI) process uses both the temperature and pressure gradients. Bottom zone of the preform is cooled, while its top zone is in hot area and there is a difference in pressures of input and output gases.

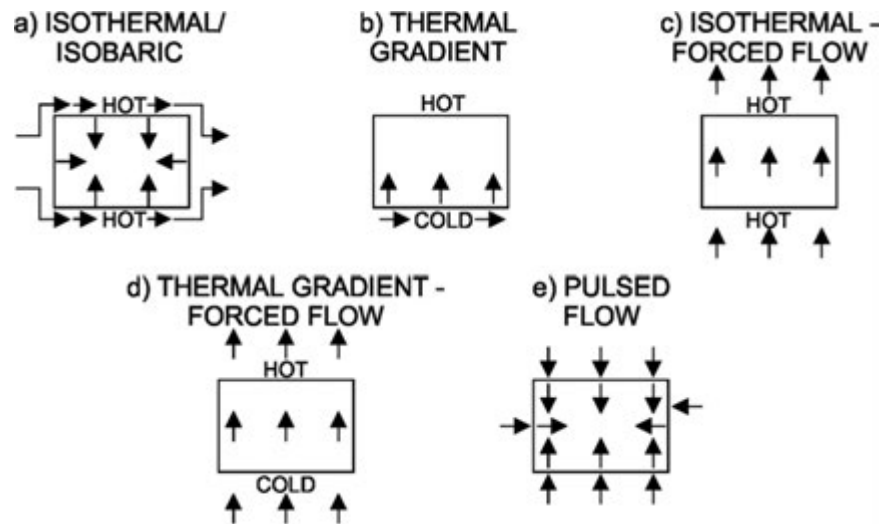


Fig. 5 Schematic representation of different Chemical Vapor Infiltration (CVI) methods.

Pulsed flow is a process that is based on the repetition of pressure cycles. Within each cycle, evacuation and introduction of the carrier gas is repeatedly done, what slightly increases the deposition time, but densification is still non-uniform (Radford and Ross, 1999).

Because of the high costs, CVI technologies are currently limited to high value products in aerospace industry, where production costs of that level are justified.

Processing of Powders, Particles, Platelets and Whiskers

Composite reinforcements can be of different forms, sizes and chemical compositions. For majority of production processes, it is necessary to supply reinforcements separately from the matrix. Materials in a form of powder make one of the major drivers in economy today, because powders are used in versatile industries. For example, production of advanced ceramics, only in USA, in 2013, consumed powders in total market value of around \$1 billion, \$16.2 billion in 2018 and is expected to reach \$24.5 billion by 2023. For CMCs, reinforcing phases are commonly in one of the following forms: powder forms of particles and platelets (particles constrained to one dimension, in a shape of thin oblate spheroids, like clay particles or SiC in MoSi₂ matrix), and whiskers and fibers which are long forms of reinforcements. Advanced CMCs also include hybrid composites and nanocomposites (with size of the reinforcements less than 100 nm).

Main production methods for ceramic powders are (Chawla, 2019; Carter and Norton, 2013; Bengisu, 2001):

- (1) Mechanical,
- (2) Chemical,
- (3) Vapor phase.

In mechanical methods, usually natural materials in a form of grains are reduced in size and pure material is separated to proceed with final milling that finally produces particle of certain sizes. It is widely used low cost method and within one fraction, particles commonly have limited range of sizes. Purity of such powders are suitable for some applications (like in construction), but for composites that require highly pure powders, some other methods are more used. Chemical methods usually consider sol – gel processing and they enable highly precise control of purity, as well as particle morphology. These methods are widely used for ceramic composites. Vapor phase methods are costly but they can produce nanoparticles in a range of 1–10 nm diameter.

For advanced ceramic composites, several powder properties are desirable such as: high purity single phase material, small particle size (<1 μm), narrow distribution of particle sizes in a powder, spherical or equiaxed shape of particles, without agglomeration. This is rather difficult to achieve due to many reasons, and such ceramic powders are expensive, thus additionally contributing to the high cost of CMCs. In reality, powders have complex structure, because they consists of single particles, agglomerates (clusters of particles), granules (large agglomerates with 0.1–1.0 mm diameter), flocs (clusters of particles in a liquid solution), colloids (very fine nanometer size, colloidal particles in a liquid solution), and aggregates (coarse constituents, usually larger than 1 mm), depending on their production technology and storage conditions. Large agglomerates are usually formed in a presence of the binding agent that is commonly added for CMCs.

Standard mechanical processing of powders is ball milling (dry or wet), wherein rotation of the barrel filled with raw material and very hard balls (alumina, zirconia, tungsten carbide, diamond) produces shearing and crushing of the powder and makes finer particles. Ball milling cannot produce particles below 0.1 μm. Another common method is spray drying where fine droplets of the solution are sprayed into a chamber where it is dried and powder is collected. Spray drying can produce particles below 0.1 μm,

but they are usually agglomerated. Sol – gel processing can produce very fine particles, and it is commonly used for thin films and fibers. Powders can be made from solution, by precipitation, where clean room and homogenous nucleation is essential, because otherwise, it can produce large agglomerates, including impurities. Unlike oxide powders that are commonly derived from natural materials, non-oxide powders often do not exist in nature. For these powders, various chemical routes are used to produce them. Advantage of direct chemical reactions is that they can produce wide range of particle sizes, and shapes, also including micro- and nanoparticles. Vapor phase methods are expensive because they use special chambers for gas evaporation (often involving plasma reactor), but they produce high purity powders, with discrete and non-aggregated particles of narrow size distributions (including nanoparticles). Also, vapor phase processing can be used for production of either oxide or non-oxide powders. Traditional production process of Al_2O_3 powder is the Bayer process (Bengisu, 2001). ZrO_2 powder is usually produced from natural raw materials, by chlorination-thermal decomposition, lime fusion, or alkali oxide decomposition (Bengisu, 2001).

Beside particulates (particles and platelets), the most commonly used form of reinforcing phases are long forms: fibers and whiskers (short fibers). Ceramic fibers and whiskers are used also in metal matrix and polymer matrix composites, not just in CMCs. Whiskers have short length (typically around 10–50 μm) and diameter usually less than 1 μm (0.05–10 μm). Ceramic whiskers are usually fibrous single crystals with very high strength and low density. Since they are single crystals, they mainly lack impurities and imperfections (such as dislocations, porosity, vacancy clusters or twins), what makes their strength up to theoretical limits. Their physical and mechanical properties are directly related to the production process. Whiskers are produced by vapor-phase reactions, vapor-vapor reactions (chemical vapor deposition, CVD), vapor-liquid-solid (VLS) method, growth from melt solutions, growth from gels and by hydrothermal growth (Chawla, 2019; Bengisu, 2001). Al_2O_3 whiskers are produced from molten aluminum or TiAl_3 . SiC particles and whiskers are produced from rice husks.

Glass fibers were the first ceramic fibers commercially used since 1940s. Glass fibers have been widely used as reinforcements in structural composites (elements of boats, airplanes, chemical tanks, window frames), insulation fabrics, high-temperature filters and many more. Traditional method of glass fibers preparation is well established and involves melting of raw glass mixture, spinning to form fibers, quenching, sizing and packing them into bundles. However, ceramic fibers other than glass ones require very high temperatures, often more than 2000°C, and they are traditionally produced by the following methods: (1) from slurry (alumina fibers); (2) by sol–gel processing (zirconia fibers); (3) by chemical vapor deposition (CVD) (SiC fibers) and (4) from polymer precursors (SiC and carbon fibers).

Carbon fibers are among the most used materials in many industries nowadays. Global market for carbon fibers is enormously large. Some statistics indicate market size of \$4.7 billion in 2019 and projected to grow to \$13.3 billion by 2029, based on increasing demands from aerospace, defense, automotive, and wind energy industries, according to Markets and Markets reports. Carbon fiber market includes raw materials (PAN, pitch, rayon), and fibers (virgin, recycled) and their applications comprise composites and non-composite materials. The same reports indicated that SiC fibers market was \$230.5 million in 2016 and that it will grow to \$1113.3 million by 2022, due to demands from aerospace, defense, energy and many other industries. SiC fibers market comprises continuous fibers and woven cloth.

Carbon fibers are made by carbonization of precursor fibers and graphitization at high temperatures. The process usually involves: (1) fabrication of precursor fiber, usually by dry, wet or melt spinning and drawing or stretching; (2) stabilization treatment to prevent melting; (3) carbonization – heat treatment and (4) optional heat treatment (graphitization) for improvement of properties. Major precursor used for fabrication of carbon fibers is polyacrylonitrile (PAN), but it can be derived from cellulose, rayon, pitch (aromatic hydrocarbons, produced from crude oil, coal or plants), polyvinyl alcohol, polyimides, polyethylene, polystyrene and phenolics (Chawla, 2019; Bengisu, 2001). SiC fibers can be produced via chemical vapor deposition (CVD) or pyrolysis of polymeric precursors. These two methods are usually applied for production of non-oxide fibers. Alumina fibers are produced by sol – gel technique: precursor fiber that is later oxidized to form alumina fiber is made by spinning from viscous gel. This concept can be applied to oxide fibers.

Within inert environment, carbon fiber has excellent properties at high temperatures, but in oxidizing environments (air) and above 400–450°C, there is an issue with oxidation, whereas SiC fiber starts with oxidation above 1300–1400°C (Bengisu, 2001). Non-oxide fibers, such as ceramic fibers are often coated with thin films to improve their durability and matrix/fiber interphase properties. Such coating represents a diffusion barrier since it prevents adverse chemical reactions that might occur between the fibers and matrix materials in direct contact under elevated temperatures. It is not easy to achieve a thermodynamically stable thin film on fibers, and especially for micro- and nano-fibers. Fibers are usually coated to improve wettability and corrosion resistance, but different approaches, as well as surface treatments have also been studied to improve fiber adhesion to matrix material and provide optimal matrix/fiber interphase (Naslain, 1993; Lissart and Lamon, 1997; Rebillat *et al.*, 2000; Naslain, 2004; Hasegawa *et al.*, 2000).

Current research is aimed at different materials that can be used as matrix/fiber interphase, such as pyrocarbon (PyC), or boron nitride (BN) (Vijay *et al.*, 2020; Fella *et al.*, 2020; Zou *et al.*, 2020; Jacques *et al.*, 2013), or alumina combined with borosilicate (Carminati *et al.*, 2021). Al_2O_3 coatings on carbon fibers by using atomic layer deposition (Militzer *et al.*, 2017), and thin films of polysilazane (Azarnoush and Raj, 2020) or YPO_4 (Boakye *et al.*, 2021) on SiC fibers have been studied. Multilayered SiC-TiC interphases at nanoscale were investigated on Nicalon fibers (Jacques *et al.*, 2013). Effects of the interphase thickness on the mechanical strength and interfacial bonding strength are important and need to be optimized (Zou *et al.*, 2020). Interphase materials react with both fibers and matrix materials and often form different interphase material (Boakye *et al.*, 2021).

New promising reinforcement for CMCs is graphene that has been studied as addition to composites either in a form of platelets or thin layers (Zhou *et al.*, 2020; Huang and Wan, 2020). Graphene nanoplatelets have exceptional electrical and thermal

properties that can significantly improve conductivity of the composite structure. Preparation of stable nanoplatelets of graphene has been established (Geim and Novoselov, 2007; Novoselov, 2004). Nanoparticles of graphene need to be homogeneously dispersed throughout the ceramic matrix, in order to enhance its properties. Low cost solution is ball milling, but colloidal processing and some novel sintering techniques are also used and investigated (Zhou *et al.*, 2020). One of the research challenges is to solve the problem of graphene degradation and agglomeration within the matrix. Comprehensive review of processing routes and properties of graphene (including available commercial forms of graphene) and production technologies of graphene/ceramic composites, as well as their mechanical, electrical and thermal properties, are given in (Huang and Wan, 2020; Nieto *et al.*, 2017).

Additive Manufacturing (AM) in Production of CMCs

In 2016, GE Aviation used 3D printing for fabrication of jet engine parts, with ceramic-based materials and they showed superb properties (25% lighter in weight than previous material; more simple and new design that was enabled by 3D print – intricate cooling pathways and support ligaments providing approximately five times higher durability vs. conventional manufacturing), thus strongly indicating that additive manufacturing (AM) should be further investigated for production of components made of CMCs. Additive manufacturing makes 3D element layer by layer, starting from the powder or liquid raw material, also enabling custom design of porosity within the bulk. It is very suitable method for deposition of gradual layers with different grain sizes, and different materials, as well as composites reinforced with different phases including micro/nano particles. However, AM technologies are still under study because many of the significant influences on the quality of the final part are still not understood.

Additive technologies for ceramics can be categorized into three groups, as: (1) slurry – based technologies (stereolithography, SL; digital light processing, DLP; two-photon polymerization, TPP); (2) powder – based technologies (3D printing; selective laser sintering, SLS; selective laser melting, SLM) and (3) bulk solid – based technologies (laminated object manufacturing, LOM; fused deposition modeling, FDM) (Chen *et al.*, 2019). Some of the AM technologies that have been used for the manufacturing of CMCs are Laminated object manufacturing (LOM), Thermoplastic 3D printing (T3DP), Powder-based binder jetting (p-BJ), Robocasting (RC) or direct ink writing (DIW), and direct selective laser sintering (SLS, DLS) (Lakhdar *et al.*, 2021; Sing *et al.*, 2017).

LOM consists of stacking, cutting (outlining) and bonding of the layers of material repeatedly until the desired geometry is formed. Layers of material are ceramic green tapes, held together with a thermally-activated binder. It can be used to make SiC/SiC ceramic matrix composites, glass-ceramic composites such as $\text{LiO}_2\text{-ZrO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ (LZSA), while curved-layer LOM (a non-planar type of LOM) can be used to make CMCs with continuous fiber reinforcement. T3DP combines robocasting with FDM, for both continuous and droplet-based printing. It employs a paraffin-based liquid thermoplastic to make a suspension with ceramic powders that are ball milled, loaded into a cartridge, and finally extruded through the nozzle. This technology can be used to produce alumina-zirconia CMCs. P-BJ can be used to produce alumina-glass composites, by spreading the dry coarse ceramic powder into thin layers using a roller and then depositing droplets of binder selectively, as predefined by the software STL file. RC, also referred to as DIW, uses a nozzle to extrude a viscous ceramic paste onto a substrate. The paste dries in the air and solidifies due to the evaporation of the solvent. RC can be used to make high-porosity CMCs with short carbon fiber reinforcement and a preceramic polymer ink base. Different ceramics can be used as matrixes with RC method such as Al_2O_3 , SiC, SiC-B₄C. RC can also produce filament structures with a SiC shell and C_f core. SLS and DLS can produce a sintered ceramic material by scanning each powder bed layer with a laser. The ceramic powder itself is melted and fused without a binder, and the resulting part does not need to be additionally thermally treated. Examples of CMCs by using DLS are $\text{Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (Lakhdar *et al.*, 2021; Sing *et al.*, 2017). The SL technique uses UV light source that selectively cures predefined liquid surface (photopolymer resin), whereas the light activates polymerization process (liquid material cure into solid). DLP technology is similar to SL, in using direct light through predefined mask. SiCN ceramic composite was additively manufactured, by DLP, and by using photocurable resin with around 20 wt% of SiO_2 nanoparticles and 1 wt% of SiC nanofibers (Xiao *et al.*, 2020).

Different AM technologies have been investigated for production of good quality CMCs, like laser melting of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ that improved flexural strength and produced samples without cracks, for potential dental applications (Hegab, 2016; Wilkes *et al.*, 2013). Oxide suspensions (3Y-TZP, Al_2O_3 , ZTA) and non-oxide ones (Si_3N_4 , MoSi_2) have been investigated by using direct inkjet printing and DLP (Hegab, 2016; Cappi *et al.*, 2008). Porous TrueForm™/ SiO_2 composite showed suitability for joists and bearers (Fan *et al.*, 2008). Porous $\text{Al}_2\text{O}_3\text{/SiO}_2$ composite has been studied for water filtration and lightweight structures (Franchin *et al.*, 2017); CaSO_4 -based composites for bone implants and dental applications (Christ *et al.*, 2015); isotropic Si/SiC composite for lattice truss structures (Fu *et al.*, 2013) and armors and blades (Klosterman *et al.*, 1998); C/C composite for gears (Yi *et al.*, 2016).

Some of the major AM technologies used for metals and polymers, are not well developed for ceramics, like powder based technologies (SLS, SLM). There is a need for profound understanding of the complex interactions between the laser and ceramic particles, as well as the influence of the process parameters on the resulting quality (layer thickness, melting temperatures, etc.). Major issue in 3D printing of ceramics is related to residual stresses that can induce defects (cracks, distortions), due to thermal gradients resulting from laser heating and cooling within the ceramic (Chen *et al.*, 2019; Stojkovic *et al.*, 2010). Also, problems related to rough surface finish, large shrinkage in post-processing and undesirable porosity within the structures are yet to be further understood. For 3D printing of ceramics, slurry based technologies showed better characteristics.

Even though AM technologies have shown highly promising results, they are still in development stages from aspects of industrial quality components. All of the aforementioned technologies have their advantages and disadvantages. There are factors to consider when choosing the optimal technology for manufacturing a certain component, such as the desired density of the final

product, surface roughness, how complex is the geometry, what type of ceramics are used, the resolution that the technology can offer in relation to the size of the printed element, cost-effectiveness, etc. The density is dependent upon the mechanical requirements for the final component in terms of strength, hence is one of the most important factors. High-density requirements eliminate the option of using dry powder bed methods because coarse powders give inadequate packing density and possess low sintering activity, which leads to a high-porosity final product. Material class generally determines the possibility for application of some AM technology. Oxide-ceramics are usually suitable for AM technologies, while non-oxide and polymer-derived are more difficult to process.

Resolution and accuracy are crucial for the production of smaller parts, while less accurate but lower-cost technologies can be employed for the larger parts. When considering cost-effectiveness, equipment, material, and processing costs should be taken into account. Cost is sometimes difficult to calculate accurately because a technology may seem affordable but it needs expensive post-processing, which drives up the price. Surface finish is closely connected to the resolution. For example, poor surface finish can be a result of printing thick layers with poor adhesion, but it is also related to density in the sense of open porosity (Lakhdar *et al.*, 2021).

AM technology field for ceramics is fragmented, even more than metal and polymer solutions. There are several areas that need to be understood and adjusted to ceramic printing, among which basic governing physical and chemical mechanisms related to process thermodynamics are the key point. Some emerging ceramic technologies, such as flash sintering and cold sintering, have shown promising results that might be used in 3D printing, as well (Allen *et al.*, 2020).

Advanced Ceramics in Smart Materials

The development of structures with integrated functionalities that are able to communicate and interact with their environment, and react accordingly to external stimuli has been applied in several areas but are still far away from wide applications. Transport industry is one of the major drivers of economies comprising extensive lists of related systems and elements where smart and advanced materials would greatly enhance safety, stability and reliability of the vehicles: aircrafts, cars, rail vehicles and associated systems. Common problem in all of these fields is related to systems and elements working in extreme conditions and environments, with additional requirement to create lighter vehicles with less maintenance. Many elements are commonly subjected to high and impact loads, aggressive corrosive environments, sometimes under highly elevated temperatures that can change from very low to very high in cycles. At the same time, these systems are usually highly responsible for the human safety and reliability of the vehicle, such as the brake system. It is of the utmost importance to design these vehicle systems and elements with great care and considering all possible sources of failures and means to prevent and control the damage.

Novel material structures and smart materials with incorporated functionalities have shown great promises. However, many of the smart functionalities or advanced structures are not practically feasible yet even with the strong theoretical and lab proofs of concept. Also, many of the material properties have been studied only in lab environments and with very limited scope of influential factors. There is a strong need to investigate the development routes of advanced material structures and functionalities aimed to address specific industrial needs and facilitate the implementation of smart materials in real system elements.

Smart ceramic behavior has been shown such as crystallographic transformation of zirconia (Zr) due to external stress that can arrest cracks (Hu *et al.*, 2012; Truskinovsky and Zanzotto, 2002). Self-healing of the silicon carbide (SiC) component in CMC has been studied (Shan *et al.*, 2020; Quemard *et al.*, 2007). However, even with excellent results showed by these materials, there is a lack of comprehensive research related to different reinforcements and resulting behavior, as well as processing routes and their work in functional environments – real systems. Additional motivation is development of these materials for additive manufacturing (AM), especially for 3D printing because of the great interest expressed by different industries. Smart surfaces can be also created by different surface modifications, like coatings or controlled surface texturing. For example, high friction surfaces can be fabricated by mimicking the gecko skin, that is, by creating numerous micro fiber arrays similar to nanoscopic hairs on the gecko.

For reliable vehicle components, significant efforts have been invested in damage sensing, prevention and control by using different sensors within the vehicle, especially in relation to the brake systems. Traditional sensor system is based on electrical circuits connected to the brake system to inform the user when it needs replacements. Thin layer is designed within the brake pad to trigger the electric current when the substrate becomes visible due to surface wear. But novel developments in application of magnetic nanoparticles opened up new avenues in development of smart components. One of the commercially applied systems, shock absorber with magneto-rheological fluid is based on magnetic micro-particles within the oil that provide almost instantaneous adjusting of the damping properties to the road profile (in milliseconds) thus resulting in a very smooth driving. It is proven that friction coefficient can be significantly influenced by the application of external magnetic field. Biomimetic structures and smart surfaces have proven exquisite results in different applications. One of the recent result in biomimicking the natural structures is magnetic damage sensing simultaneously accompanied with self-repairing of surfaces, by using magnetic nanoparticles within thin layers that altogether formed magnet-polymer composite (Ahmed and Ramanujan, 2015).

Novel functionally graded materials (FGM) represent the concept developed to introduce gradual change of properties within the bulk and very often to mimic natural structures. Considering that FGMs are gradient by their nature, it is very suitable to incorporate layers that will provide damage sensing and self-repair upon crack initiation. FGMs exhibit uniform distribution of stresses, crack arresting ability and better adhesion of coatings, but they can also enable lower consumption of raw materials by introduction of designed porosity into the bulk, directly meaning lighter products. Additionally, introduced porosity is proven way

to provide shock absorption and vibration suppression. Open porosity also enables infiltration of completely different materials (fluids, nanomaterials) within the structure, thus offering additional functionalities. Research results showed that FGM structure applied in shafts had resulted also in vibration suppression, what is very important for many elements, like space frames or sides in vehicles. New nanomaterials offer extension of the FGM concept to thin films and surface modifications in nano domain. Functionally graded materials and composites can be deposited as thin layers on less qualitative substrate, such as cermet coatings on steel substrate to create smart surfaces (Ghasali *et al.*, 2020; Zhou *et al.*, 2018; Sarkar *et al.*, 1997; Grujicic and Zhao, 1998). This method has promised good results in providing steel elements with superior qualities without replacing steel with more costly materials. There are four traditional processing routes for FGMs: powder processing, CVD, high-temperature synthesis and plasma spraying, but new methods have been extensively studied like friction stir processing (FSP), laser assisted modifications and others, mainly aiming at low cost solutions (Saleh *et al.*, 2020; Parihar *et al.*, 2018).

Cermet is a composite material consisting of ceramic and metal materials, usually with less than 20% of metal content serving as the binder for ceramic oxide, boride or carbide. Cermet combines good ceramic and metal properties: hardness, ductility, high temperature resistance and exquisite wear resistance to erosion. Accordingly, functional nanolayered cermet coatings (e.g., WC-Co or WC-Co-Cr functionally graded coatings) can improve both the properties and performance of solid one-phase structures, as well as protect the substrate material. Modification of steel surface, such as laser modifications or shot peening, can contribute to better coating adhesion. If nanolayers of cermet films with different grain properties are deposited on such modified surface, the joint structure can be tailored to provide uniform distribution of stress and strain without discontinuities. WC-based cermet coatings can replace traditional hard chrome films related to many environmental issues, and especially their toxicity. They are wear resistant also in humid corrosive environment. Spray techniques used for deposition of cermet films are very suitable for investigation of different grain sizes effects (Vencel *et al.*, 2011). Submicron size WC-based particles in sprayed cermet films greatly influence wear and corrosion properties of the coated surface but underlining mechanisms are yet under investigation (Yuan *et al.*, 2016).

Nanostructured WC-Co coatings showed promising enhancement of performances related to extreme wear and corrosion, as well as fracture toughness, especially in combination with steel substrates (Baumann *et al.*, 2021). However, different influential factors still need to be investigated, such as effects of grain size, nano and/or micro WC grains, content of binder phase, diffusion of hard phase to the binder, on hardening and ductility, as well as stress - strain distribution upon loading and cracks initiation and development, especially in new functionally layered structures (Srinivas *et al.*, 2019; He *et al.*, 2018). High velocity oxy-fuel spraying (HVOF) is established as the best technique for cermet coatings, but at the same time it is very suitable for depositing different layers with variation of grain sizes to provide FGM structure. Layered structure will prevent formation of cracks along the coating and increase the durability. Thermally-sprayed FGMs for wear and corrosion protection have been a subject of research in recent years that might lead to completely new applications in different fields (Fauchais *et al.*, 2011; Lima and Marple, 2007).

Surface texturing prior to the film deposition (like shot peening) can provide compressive stresses close to the interface, to relieve high tensile quenching stresses which is rather large in pure WC-Co, and further minimize the risk of nanolayers delamination. Accordingly, smooth gradient stress distribution can be provided within FGM, from tensile at the top layer to small compressive stresses within steel-rich layers. This way FGM will function as the damage damping structure under severe contact loading, in both cases of static and dynamic loads. FGM structure exhibits superior ability to control the development of cracks. Cracks can appear in the cermet top layer and be further arrested or deflected in the underlying layers. One of the issues in HVOF sprayed steel is related to rolling contact fatigue loading (Valarezo *et al.*, 2010).

Apart from investigations related to properties and possible applications of FGMs, significant efforts have been devoted to their production technologies (EL-Wazery and EL-Desouky, 2015). So far, powder metallurgy and thermal spraying are established processing routes, but new technologies are emerging, among which additive manufacturing (AM) again offers unprecedented levels of freedom to design complex structures and material combinations (Li *et al.*, 2020).

Surface Composites by Friction Stir Processing

One of the established technologies for surface modifications, Friction Stir Processing (FSP), has recently started to be used for fabrication of surface ceramic composites (Bharti *et al.*, 2020; Weglowski, 2018; Sudhakar *et al.*, 2018; Bhavya Swathi *et al.*, 2019; Rathee *et al.*, 2018; Sharma *et al.*, 2015). FSP is technology derived from Friction Stir Welding (FSW), as rather new approach in joining materials in aerospace and transport industries. These technologies use the friction force energy to realize joining of the two materials in contact, whereas governing mechanisms are mixing and alloying of chemical elements under the influence of increased temperatures in localized zones. In this way, thin zone of the third material is formed that makes a firm bond between the initial materials that were in contact. Technology is rather simple, but it is still under study, due to complex interrelations at micro and nano scales during the FSW process. FSP is efficient technology to form ceramic-based coatings on metal surfaces, but can be used also with other material combinations. Schematic representation of the friction stir processing (FSP) is shown in Fig. 6.

Ceramics are added in powder form prior to FSP process, onto the metal surface, usually by using one of the three methods: grooves or holes on the substrate surface or cover plate. The special tool rotates and generates extensive plastic deformation within the surface layers, with increase of energy by friction. The forces acting by the tool rotation is causing the surface particles to disperse within the matrix. Surface and subsurface zones of the material are subjected to high frictional heat, what results in localized stirring of particles of all materials that are in contact (metal substrate and ceramic powder). Material flows from the

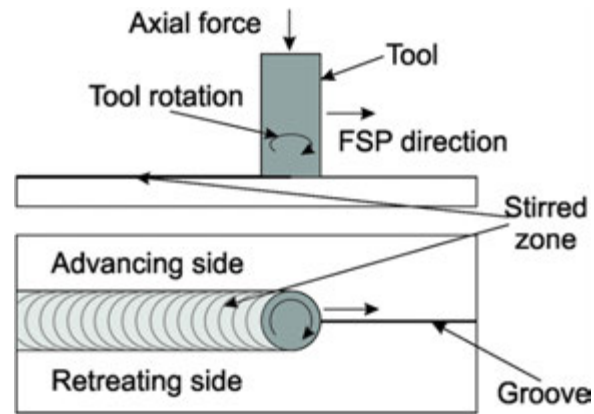


Fig. 6 Schematic representation of the friction stir processing (FSP) for ceramic coatings.

retreating side (RS) to the advancing side (AS). After the FSP tool leaves the contact zone, material is cooling and hardening occurs, with defect free stirred zone, thus forming the composite structure on the substrate surface. Composition of the coating consist of materials in contact (substrate material and powder material that was on the surface prior to FSP).

Different composite coatings have been deposited by FSP, whereas majority of them were based on SiC or Al_2O_3 , and focused on tribological applications. SiC based coatings usually provide increased hardness and better wear resistance than the substrate, like in the case of Al-SiC composite (Sharma *et al.*, 2019) or the hybrid (SiC + MoS_2)/A356 composite (Alidokht *et al.*, 2011). Presence of SiC particles in SiC/AZ91 composite provided fine and homogenous grain structure (Asadi *et al.*, 2010). SiC/Cu composite coating on copper showed higher wear resistance than pure copper and slightly increased friction coefficient (Barmouz *et al.*, 2011). Microhardness of SiC/AA5052 composite was improved for 55% and wear rate was reduced by 10 times in comparison to pure 5052 Al (Dolatkhah *et al.*, 2012). Grain size and volume fractions in Al_2O_3 /AZ31 and Al_2O_3 /AZ91 composites have been studied and small size of grains in ceramic powder was more favorable for hardness increase (Azizieh *et al.*, 2011; Faraji *et al.*, 2011). Recently studied AZ91/ B_4C composite also showed that smaller grains resulted in better improvement of the coating microhardness (Singh *et al.*, 2018). Hybrid (SiC + Al_2O_3)/AA1050 composite coating with 20% of Al_2O_3 and 80% of SiC showed exceptionally good wear resistance (Mahmoud *et al.*, 2009).

Recently, FSP has been investigated for fabrication of thin biomedical ceramic coatings (Gu *et al.*, 2019; Ding *et al.*, 2019; Rahmati and Khodabakhshi, 2018; Bahl *et al.*, 2017). Thin bioactive ceramic coatings on metal alloys are of interest for biomedical implants, since they can improve corrosion properties and bioactivity of biomedical Ti alloys (Bartmanski *et al.*, 2019). Electrophoretic deposition that is usually applied for such coatings can be combined with FSP, like in fabrication of Ti-CaP biomedical coating on Ti6AL4V substrate (Farnoush *et al.*, 2013). In final stage, nano-hydroxyapatite coating was deposited on Ti-CaP, thus providing bioactivity. This multi-layered coating on Ti6AL4V also provided better corrosion resistance, which is one of the issues in Ti-based biomedical implants. TiO_2 /Ti-35Nb-2Ta-3Zr anti-corrosion micro/nano-composites deposited on Ti-35Nb-2Ta-3Zr was stable and showed significantly improved anti-corrosion properties (Gu *et al.*, 2019). Nanoparticles of hydroxyapatite was dispersed in Ti surface by FSP and resulting thin coating showed increased strength and hardness, but the interfacial bonding between hydroxyapatite and titanium was not so good (Rahmati and Khodabakhshi, 2018). Investigation of FSP processing parameters with titanium substrate and TiN particles showed that their control can govern the properties of the resulting surface coating (Bahl *et al.*, 2017).

Recent Advances and Future Research

Processing of CMCs and development of new compositions, including hybrid composites, have been a significant focus of research during the last 20 years. Different processing techniques have been studied and influential parameters that can optimize and reduce the cost of CMCs, as well as improve their properties. Production technologies have essential influence on fiber properties, including their thermo-oxidative stability (Shestakov, 2020) or mechanical and thermal properties (Pirzada *et al.*, 2021). Formation of different hybrid CMCs like ZrB_2 -SiC and HfB_2 -SiC with addition of TaSi_2 or Y_2O_3 , has been studied in scope of recent European research projects (Justin *et al.*, 2020). Production of complex shapes has been a problem in CMCs, as well as their joining technologies and some new methods are studied, like gelation of slurries (Almeida *et al.*, 2020) or new additive manufacturing (Lakhdar *et al.*, 2021; Li *et al.*, 2020; O'Masta *et al.*, 2020). New experimental research of sintering temperatures above 1750°C indicated that new phases might appear during the fabrication that can significantly influence the final composite properties, like in the case of cubic boron nitride (cBN) ceramic matrix (Slipchenko *et al.*, 2020). Traditional methods like reactive melt infiltration (RMI) have been studied for production of hybrid composites. By introducing porosities in the preforms, 3D-Cf/HfC-SiC-based composites were fabricated (Jiang *et al.*, 2021). In situ fabrication of CMCs has gained important attention, like combustion-based production of SiC_{nw} -reinforced SiC matrix, with single-crystal SiC nanowires (SiC_{nw}) on the surface of carbon fibers (Vorotilo *et al.*, 2020). Development of ultra-high temperature CMCs for

structural applications in corrosive environments at temperatures above 1600°C (rocket and hypersonic vehicle components) is focused on Zr, Hf, Ti, with addition of TaC (Binner *et al.*, 2020).

Some materials are proven in a lab to have extremely good properties for highly demanding structural applications, like MAX phases. Hexagonal forms of carbides and nitrides with layered structure belong to a group of materials named MAX phases. There are more than 150 different compositions. They exhibit exceptional properties at high temperatures (oxidation resistance up to 1400°C in corrosive atmosphere, thermal shock resistance, self-crack healing, and high damage and radiation tolerance). However, their commercial applications have been restricted, due to unavailability of highly pure commercial powders and processing techniques are of the great importance (Gonzalez-Julian, 2021).

Design of composites inspired by nature indicated some less costly solutions of composite processing and fabrication, like mixing different phases (Bouville, 2020). If the fibers of the same material are used to form the composite structure by contacting each other by different plane surfaces, it can be tailored in such a way to provide non-brittle behavior (Nikonovich *et al.*, 2021). If local resonance and strain rate effects and cellular structure are introduced in the structural design, resulting material can show extreme hardness and ultra-high resistance to cutting (even to waterjet cutting) and high deformation capability (Szyniszewski *et al.*, 2020). Some new compositions of biomorphic Si/SiC composites have been made with wood-based materials, by using low cost production technologies and achieving near-net shape, also with possibility to tailor the microstructure, and composite properties (Arellano-López *et al.*, 2005). Additive manufacturing has been intensively studied, since it is expected that it will reveal low cost solutions to different combinations of composite constituents, along with possibilities to produce very complex shapes and structures, including porous structures of CMCs (Lakhdar *et al.*, 2021; O'Masta *et al.*, 2020).

Nanotechnologies also contributed to the development of CMCs. Carbon nanotubes (CNTs) can improve ceramic matrix composites in terms of mechanical and other properties. However, for CMCs, their toughening and load-bearing properties are still under study. CNTs have many favorable properties such as high strength and elastic modulus. They are also very thermally and chemically stable. Achieving uniform dispersion of CNTs in the ceramic base can be an issue, due to a likely damage during the process and agglomeration. Interfacial incompatibility could also be a negative factor. These are obstacles that need to be solved for the production to be scaled up. Multi-wall carbon nanotubes (MWCNTs) have been studied as possible reinforcements, also with thin coatings (Liang *et al.*, 2017). Conventional methods such as wet mixing of CNTs with ceramic powder, beads milling and jet milling are not fully suitable, but novel methods such as the aqueous colloidal approach, which uses electrostatic forces to uniformly disperse charged CNTs and ceramic nanoparticles in water, could prove successful (Estili and Sakka, 2016).

Discovery of graphene with exceptional properties opened up extensive research related to its applications, also in relation to CMCs (Nieto *et al.*, 2017). Research groups experimented with addition of graphene in CMCs, and studied new processing routes for such composites (Sun *et al.*, 2020). Ambient flash sintering was proposed as efficient method to produce zirconia based composites with graphene oxide (Xiao *et al.*, 2021) or with graphene nano-platelets (Fele *et al.*, 2020). Processing routes and their influence on mechanical properties of composites with alumina matrix and graphene reinforcement, are at the beginning of development (Shah *et al.*, 2020). New less energy intensive processing routes will enable more freedom in design of CMCs (Biesuz *et al.*, 2020).

Conclusions

Processing routes have essential influence on the final composite properties. Among traditional production technologies, powder processing accounts for approximately 50% of all technologies. However, more suitable technologies are liquid phase and especially gas phase processes, from aspects of microstructural and mechanical properties at micro- and nano-scales. Major drawback of all production technologies of CMCs is very high processing temperatures. Some recent studies promise to enable technologies with lower temperatures and better control of the composite properties, among which are: Microwave (MW) sintering, Flash sintering, Spark plasma sintering (SPS), Flash cold sintering, Cold sintering process (CSP) and Cold sintering (CS), together with Additive Manufacturing (AM).

Production routes strongly influence the characteristics of the reinforcements (physical, chemical, and mechanical properties), which further determine composite properties. Significant efforts have been devoted to the processing of powders, particles, platelets and whiskers, methods of their coating and structural design of matrix/reinforcement interphases.

Current research trends promise to enable smart behavior, including crack arresting and self-healing behavior, functionally graded materials (FGM) and nanostructured surface coatings. Friction Stir Processing (FSP) has emerged as low cost solution for depositing CMC coatings on metal surfaces. Novel reinforcements like graphene and carbon nanotubes (CNTs) promise further improvements of CMCs.

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Manufacturing of Fiber-Reinforced Ceramic Matrix Composites by Filament Winding and Freeze Gelation

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Introduction

Monolithic ceramics are well known for their resistance to high temperatures, their chemical and oxidative stability and elevated hardness and compressive strength. Monolithic ceramics find applications in various fields, such as in cutting tools, furnace components, medical implants and bearings. In comparison with metals, they present lower density and intrinsic oxidation resistance. On the other hand, monolithic ceramics present higher brittleness and low fracture toughness, which are the main drawbacks associated to their utilization ([Newman and Schäfer, 2001](#)).

In order to improve ceramic brittleness and fracture toughness, fibers are commonly employed as reinforcement. Fiber-reinforced ceramic-matrix composites (CMC) started being significantly studied in the early 1980s ([Cox and Zok, 1996](#)). These materials, specially oxide based CMC, provide high strength, toughness, notch insensitivity, refractoriness, and environmental stability at high temperature applications where metals are usually limited by their melting temperature and monolithic ceramics are limited by their low damage tolerance. Furthermore, this class of materials can be designed to induce macroscopic inelastic deformation mechanisms in either tension or shear ([Simon and Danzer, 2006](#); [Simon, 2005](#); [Russell-Floyd et al., 1993a](#)). These characteristics make them promising materials for applications such as thermal protection systems for reusable spacecraft, hyper sound missiles, combustion chamber, diffuser and exhaust from aircraft engines and stationary gas turbines.

The reinforcement provided by the fibers and consequently the material fracture toughness shall be adjusted by crack deflection and energy dissipation of the material. In CMC, the crack propagation is achieved along the fiber matrix interface leading to the pull-out effect. The pull-out effect can be designed either by using weak interface composites (WIC) or weak matrix composites (WMC). The WMC concept is characterized as a fiber dominant behavior, where the fiber interface is not particularly conditioned to allow debonding and the crack propagation is accompanied by energy dissipation through a porous matrix. The WIC concept is governed by a weak fiber-matrix interface, in which the energy dissipation occurs from a gap or weak fiber-matrix interface generating the fiber pull-out ([Simon and Danzer, 2006](#); [Koch et al., 2008](#)).

Within the class of ceramic matrix composites C/C (carbon matrix reinforced with carbon fiber), C/SiC (silicon carbide matrix reinforced with carbon fiber), SiC/SiC (silicon carbide matrix reinforced with silicon carbide fiber) are most commonly found. Carbide based composites have already achieved a high manufacturing and design level and are already industrially produced given their very good mechanical properties. Such composites can be found regularly in air and space applications as thermal protection systems for spacecraft, missiles, and brake pads. Nevertheless, this class of CMC presents a strong disadvantage: their low oxidation stability at temperatures above 500°C, which consequently leads to loss of mechanical performance due to embrittlement, limiting their use in air and oxidative environments. In order to use these materials at high temperature applications, expensive oxidation coatings are needed. This drawback contributed significantly to the development of oxide based CMC.

Among the promising applications for oxide based ceramic matrix composites, their use in aircraft engine and stationary gas turbines has been intensively developed in the past decades, mostly due to the demand for materials with improved performance, availability, maintainability, durability, and reduced emissions of NO_x and CO. The contributing factors are rising fuel costs, the need to minimize operating and maintenance costs and increasingly strict emission regulations. Ceramic materials have the potential to provide 30,000 h of trouble-free operation that industrial gas turbine operators come to expect. Ceramic matrix composites are very interesting for gas turbine hot section components. Their superior high temperature durability compared to metals enables higher component operating temperatures – consequently, improving fuel efficiency. Additionally, the air volume saved due to the reduced demand for hot section component cooling could be redirected to lean out the combustor primary zone and reduce the formation of NO_x ([van Roode et al., 2005](#)). The reduction in cooling air also enables higher firing temperatures, improving engine efficiency, and the incorporation of a combustor liner made of CMC would also prevent the formation of CO ([van Roode et al., 2005](#)).

With this background in mind, continuous development of oxide based CMC manufactured with different matrix systems and processing routes has been conducted mostly in Germany and in the United States. For instance, oxide based CMC are currently manufactured at Airbus Group Innovations (UMOX™), at the German Aerospace Center (WHIPOX™ and OXIPOL™), at Walter E.C. Pritzkow Special Ceramics (Keramiklech®), at the Air Force Research Laboratory (AFRL), at COI Ceramics and at the University of Santa Barbara. These materials are mainly produced with the oxide fibers Nextel™ from 3M™ Company (USA), made of alumina (Nextel™ 610) or mullite (Nextel™ 720). The ceramic matrices developed for these materials are manufactured using polymer-based slurries, water-based slurries or via sol-based slurries. Fiber infiltration and composite lay-up take place either by filament winding when continuous fibers are used or by hand lamination when fiber cloths are used.

All these developments with different combinations of manufacturing routes result in ceramic composites with different microstructures and properties. The high requirements in long term applications could, at today's development state, not yet be fulfilled. The progress achieved in the CMC field during the last 15–20 years has not yet led to broader application and has been mostly realized in laboratory scale or at research institutes where industrial manufacturing processes are not applicable. Regardless of the manufacturing route used up to the present, all these materials have not yet achieved high performance mechanical properties in respect to their interlaminar properties. These composites often present long processing times, which reflect directly in high manufacturing costs. Additionally, some of these composites contain low amounts of silicon carbide being more susceptible to oxidation.

Therefore, the necessity for alternative manufacturing routes to develop CMC is made obvious, in order for these materials to fulfill the requirements for these promising applications, overcoming the drawbacks of the actual state of the art of CMC materials.

Colloidal Technology

Sol-Gel

Sol-gel processing has brought a whole new point-of-view in the domain of glass and ceramics fabrication (Russell-Floyd *et al.*, 1993a; Pierre, 1998). Among several ways of ceramic matrix composite (CMC) production, this promising technique has proved to be viable and has gained its place in the field along the recent years.

Several near-net-shape forming techniques for ceramic components have been developed in which fluid slurries can be transformed into rigid bodies without liquid removal, called sol gel. These direct consolidation forming techniques include, among others, gel casting. Direct consolidation routes have the potential to transfer the high degree of homogeneity achieved in the slurry to the green state. Depending on the used technique, ceramic powders and colloidal suspensions can be wither aqueous or nonaqueous, and also electrostatically or sterically stabilized (Tari, 2003; Rodeghiero *et al.*, 1998).

A colloidal suspension of solid ceramic particles (sol) may be converted to a non-crystalline gel through controlled interruption of the small interparticle forces that control sol stability. The interruption of the interparticle forces in order to achieve consolidation or gelation of the sol may take place by modification of the suspension pH or changes in temperature or even pressure. The gel may then be dried and sintered (Russell-Floyd *et al.*, 1993a; Chant *et al.*, 1995; Hench and West, 1990).

In order to make use of the sol-gel process for colloidal suspensions containing fillers it is important to study the zeta potential and isoelectric point (IEP) of the particles to be used in order to know the pH range in which the suspension can be manufactured, avoiding flocculation or coagulation. The zeta potential corresponds to the electrokinetic potential of particles in colloidal systems. Its value is related to the stability of the colloidal suspension, by indicating the degree of repulsion or attraction of the charged particles in suspension. If the zeta potential is zero, attraction exceeds repulsion, meaning the particles will flocculate or coagulate. Higher zeta potential values (either negative or positive) mean that the particles are stable in suspension. The isoelectric point corresponds to the pH value in which the particles are not charged, i.e., the zeta potential is zero. At this point, the particles attract each other and coagulate due to the lack of charging and a stable suspension is no longer achieved.

Advantages of sol-gel methods over conventional ceramic processing routes include high matrix homogeneity – since the fine ceramic particles are intimately mixed in the colloidal state – the ability to prepare compositions which are difficult to achieve by conventional methods, and relatively low sintering temperatures as a consequence of the high reactivity from the elevated surface area of the gel (Tari, 2003; Rodeghiero *et al.*, 1998; Chant *et al.*, 1995; Statham *et al.*, 1998; Sigmund *et al.*, 2000). However, its major drawback is the inherent shrinkage of the gel, which occurs as it dries out during evaporation of the original solvent and during subsequent sintering. Non-reactive fillers and reinforcing fibers reduce the volume shrinkage from typically 20%–25% to levels as low as 7% (Chant *et al.*, 1995; Statham *et al.*, 1998).

Freeze Gelation

The freeze gelation process is applied when sol-gel suspensions are gelled by submitting them to temperatures well below 0°C. The use of freeze gelation overcomes many of the limitations of sol-gel processing, permitting the formation of low-cost, crack-free, typically zero-shrinkage ceramics even in the presence of high loadings of reinforcing fibers (Statham *et al.*, 1998).

The freeze gelation route can be divided in four steps: preparation of the slurry, freezing, removal of solvent, and sintering.

Ceramic suspensions are prepared as water-based sols; the ceramic filler is added in order to improve mechanical stability and reduce shrinkage. In the homogenization step, it is very important to assure the stability of the sol-gel suspension in order to avoid any segregation, which could result in density and porosity gradients in the final material microstructure. In the case of composites, the slurry is first infiltrated into fibers and then submitted to sub-zero temperatures to ensure gelation. In the case of monolithic ceramics, the slurry is submitted to sub-zero temperatures directly after homogenization and shaping (Chant *et al.*, 1995; Statham *et al.*, 1998; Deville, 2008; Scotti and Dunand, 2018).

During freezing, ice crystals are formed from the aqueous solvent of the sol with a small increase in volume caused by the transformation of water to ice. A gel is formed in the regions between the ice crystals. As freezing occurs, the particles in the slurry are rejected from the moving freezing front and piled up between the growing ice crystals. Subsequently, the frozen material is dried at temperatures slightly above ambient temperature for water removal. This step results in bulk shrinkage often below 1%,

owing to low capillary stresses associated with the relatively large and open porosity (typically 1–10 μm in diameter), which results from the nucleation and growth of ice crystals during freezing. The green body is relatively weak and must, therefore, be sintered to achieve sufficient mechanical strength. The macropores will be a replica of these ice crystals, while the micropores will be a result of sintering densification of the matrix (Chant *et al.*, 1995; Deville, 2008; Scotti and Dunand, 2018).

In order to consolidate and to prevent the gel from melting during reheating to ambient temperature, it is necessary to use a freeze sensitive sol, i.e., an irreversible sol-gel transformation. There are a variety of colloidal sols that are deemed irreversible after freezing; the majority of those are silica-based sols (Statham *et al.*, 1998; Brinker and Scherer, 1990). The silica sol is consolidated by compaction of particles, with the formation of a three-dimensional network. Two mechanisms can promote this consolidation: gelation or coagulation. The first involves the collision of two particles and the formation of siloxane bonds (Si–O–Si) under the release of water (H_2O). In the second, a clotting agent, usually an electrolyte, acts as a "bridge" between two silica particles, connecting one another.

The consolidation of the sol, either by gelation or coagulation, can be influenced by factors such as pH, size and concentration of particles, presence of electrolytes and organic liquids as well as temperature. With this property, the silica sol can be used as a binder, avoiding the use of other hydraulic binders. The strength and consolidation of the green body is, therefore, achieved by the formation of a three-dimensional network of siloxane-bound particles and not by hydration of a binder additive (Ismael *et al.*, 2006).

Several aspects and process parameters influence directly the freeze gelation process and the final material structure and properties. These aspects are associated with the colloidal silica sol, fillers, solidification, and sintering parameters.

For the sol-gel transformation, it is crucial that the particles present in the suspension are sufficiently small to remain stable in suspension and capable of relatively close packing, as the growing ice crystals concentrate the colloidal particles into inter-dendritic areas during freezing. The filler that is added to the sol influences the stability and final physical characteristics of the ceramic, such as its porosity. Hence, filler particle size and weight fraction must be adjusted in order to achieve an optimum viscosity for infiltration of fibers or casting and for the desired porosity and mechanical strength to be achieved (Russell-Floyd *et al.*, 1993a,b). The study of each component's pH and isoelectric point when adding ceramic fillers to the silica sol is also rendered important, to avoid particle aggregation during suspension preparation and to optimize slurry stabilization.

A critical stage of this process is the solidification, i.e., freezing, since the characteristics of the future porosity will be determined at this step. During the formation and growth of ice crystals, ceramic particles in suspension are rejected by the moving solidification front and entrapped between the ice crystals. The pore structure is influenced then, besides by the utilized solvent, by the freezing rate and the freezing direction applied (Deville, 2008).

The freeze gelation process results in a porosity gradient in the monolithic ceramic microstructure (Koch *et al.*, 2003; Waschkies *et al.*, 2009; Deville *et al.*, 2010, 2006, 2007). As the freezing front proceeds from the cooled surface to the interior of the slurry, a strong gradient in the porosity is observed. A uniform and texture-free microstructure with formation of ultra-fine ice crystals in the range of a few nanometers is observed in the surface closest to the freezing front. With increasing distance from the cooled surface, the pore size increases.

During freezing, the velocity of the liquid front decreases rapidly as the distance from the freezing front decreases until it reaches a steady state with an approximately constant value (Fig. 1). Consequently, the first frozen zone reveals a planar ice front where the filler particles are entrapped. The ice crystals then move progressively to a columnar and eventually lamellar morphology, with a progressive ordering of the lamella. A steady state is eventually reached and the ice crystals become continuous, running through the entire sample with a constant thickness. Fig. 1 shows an example of an alumina suspension frozen at -10°C ; the spacing between the former ice crystals increases dramatically as the ice crystal grow inside the ceramic material, away from the cooled side.

Additionally, the size of the particles in suspension influences the size of the ice crystals and, consequently, the final porosity. Fig. 2 shows the porosity of an aqueous alumina suspension frozen at a constant cooling rate of 5K min^{-1} until complete solidification is achieved. The smaller the size of filler particles, the more nucleation sites for ice crystals will be available and so several pores with smaller size will be formed (Deville *et al.*, 2010).

The main advantage of the freeze gelation process is the ability to form large or small complex-shaped near-to-net-shape components with multidirectional fiber reinforcement, either by simple casting for short fiber reinforcement, by filament winding for continuous fiber reinforcement or by hand lay-up for fabric weaves (Deville, 2008; Gilissen *et al.*, 2000; Naskar *et al.*, 2009).

Ceramic Matrix Composites

In this section, methods of fiber preform fabrication and matrix infiltration will be reported. Special attention will be given to the filament winding technique and the ceramic slurry infiltration (CSI) methods.

Fiber Preform Fabrication

Fiber preform can be classified into 2- or 3-dimensional preforms. According to the various textile techniques available, the fibers can be processed and classified through different techniques, such as weaving, braiding, winding, or stitching.

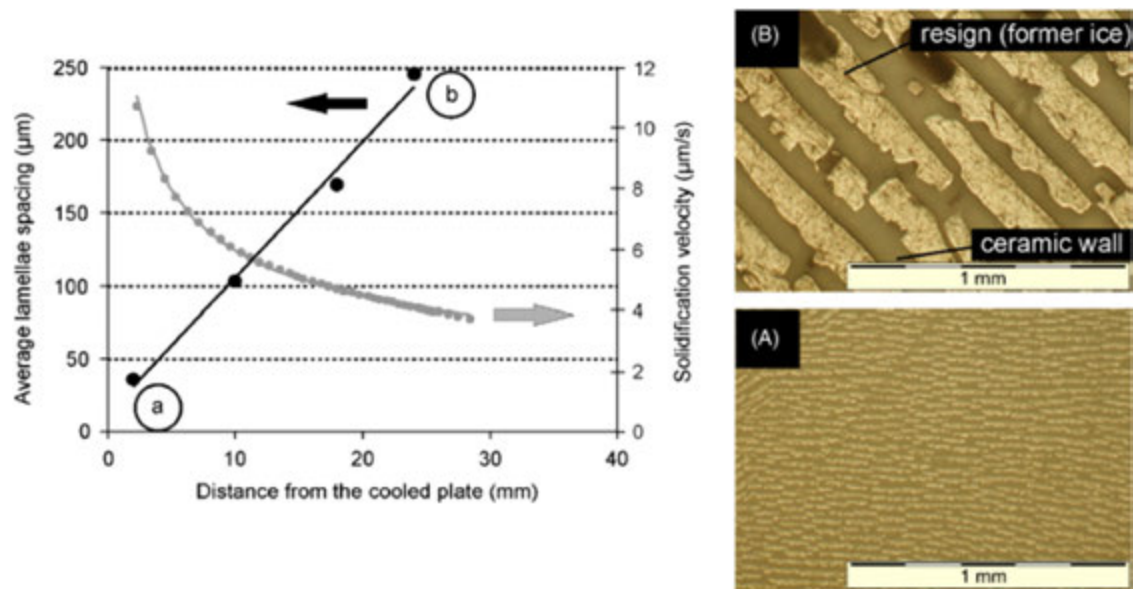


Fig. 1 Lamella spacing development during solidification (22 vol% solids loading) under constant freezing conditions of -10°C . Reprinted from Waschkes, T., Oberacker, R., Hoffmann, M.J., 2009. Control of lamellae spacing during freeze casting of ceramics using double-side cooling as a novel processing route. *J. Am. Ceram. Soc.* 92, S79–S84, with permission.

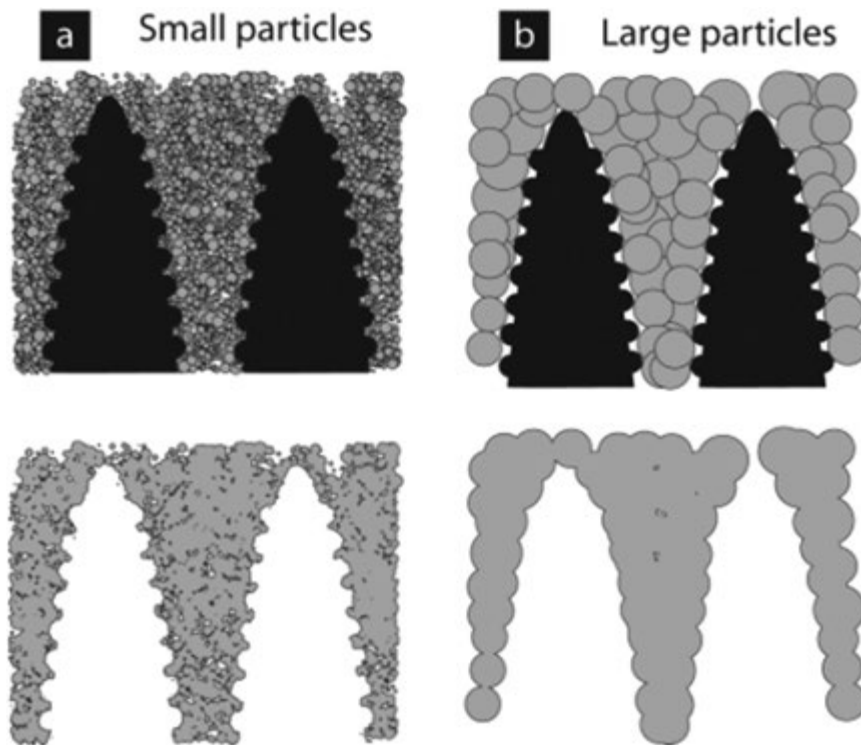


Fig. 2 Influence of particle size in structure porosity of the material. Reprinted from Deville, S., 2008. Freeze-casting of porous ceramics: A review of current achievements and issues. *Adv. Eng. Mater.* 10, 155–169, with permission.

In the weaving technique, 2- and 3-dimensional preforms can be manufactured. 2D woven fabrics are more commonly used when good in-plane properties, drapability, and large area coverage are required. Two-dimensional fabrics are commonly used in fabrication of engine nozzle structures, thermal protection systems, and other relatively non-complex hardware with relatively low out-of-plane loading requirements. The 3D structure has excellent damage tolerance, improved shear property performance and

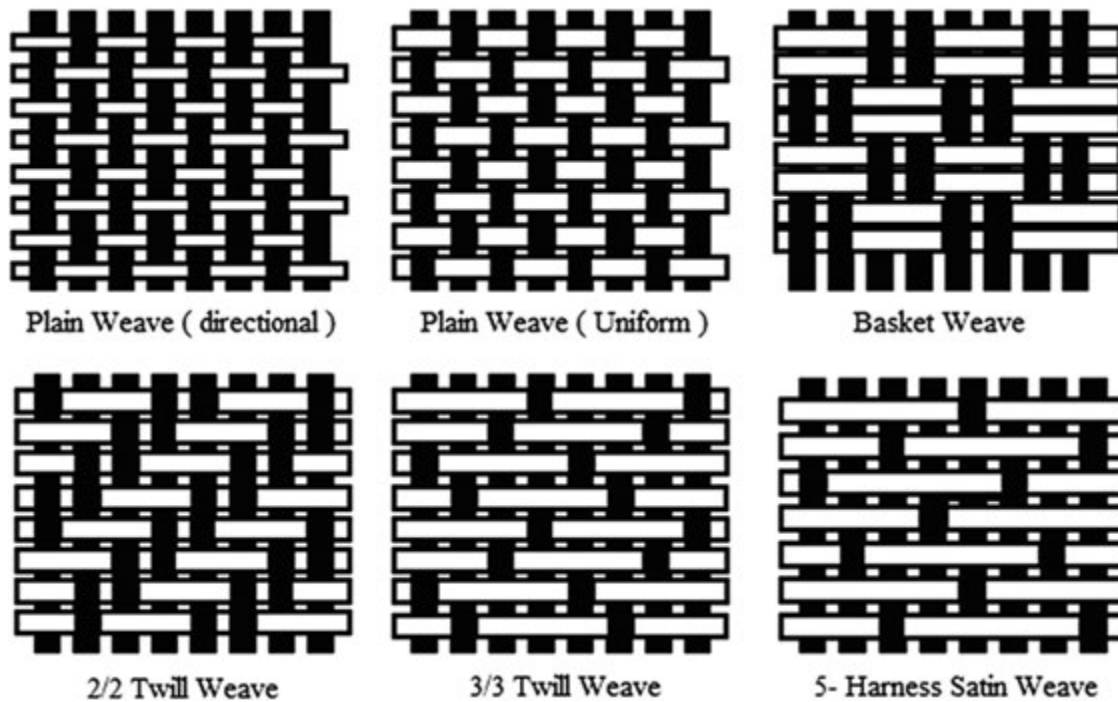


Fig. 3 Different weave architectures available for fiber preform manufacture. Reprinted from Khatavkar, N., Balasubramanian, K., 2016. Composite materials for supersonic aircraft radomes with ameliorated radio frequency transmission-a review. RSC Adv. 6, 6709–6718, with permission from the Royal Society of Chemistry.



Fig. 4 Robot-assisted circular braiding machine at Airbus Group Innovations, Germany. Image provided by Airbus.

designed specific strength and stiffness. The fabrics can be divided into different bond types, each with a different weaving sequence between weft and warp thread (Fig. 3). Generally, when fiber deflection is increased, the form stability and the handling of fabrics are improved. On the other hand, the mechanical properties of composites are decreased.

Another way to produce fiber preforms is via braiding. Its main advantage is its ability to fabricate textile preforms with different lengths, diameters and different fiber architectures. Braiding has been more commonly used with carbon fibers, although research developments with ceramic fibers have already been done. In Fig. 4, a circular braiding machine from Herzog Machine Factory GmbH & Co KG, Germany is shown. It has 144 bobbins and a fully automated handling robot from KUKA Robots GmbH, Germany.

The filament winding technique can produce preforms with different geometries, with considerable geometrical accuracy, reproducibility and generally high fiber volume fractions. Additionally, this technique allows the fabrication of rotationally symmetric products, such as pressure vessels, shafts, containers, pipelines, radomes, turbine thrusters, and combustion chambers. Differently from other techniques, in filament winding, slurry infiltration is done simultaneously to fiber lay-up.

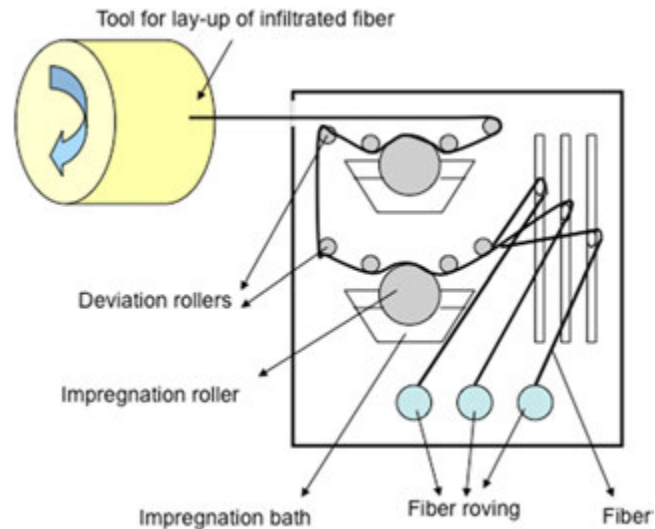


Fig. 5 Filament winding process scheme exemplifying the fiber roving infiltration and lay-up at a rotating mandrel. From the author.



Fig. 6 Robot assisted 6 + 2-axis filament winding machine at Airbus Group Innovations. Image provided by Airbus.

The filament winding process consists in the infiltration of fiber bundles through immersion into a matrix suspension bath. The fiber bundles are conducted through an eye under controlled tension and wound onto a rotating mold (mandrel) in a prescribed path. More sophisticated machines allow winding of up to three fiber bundles simultaneously, as well as the use of two infiltration baths for more homogeneous slurry infiltration into the fiber inner filaments (Fig. 5).

For better performance and quality of the final wound component, several aspects during filament winding must be respected. Some of these aspects are:

- (1) the control of the tension in the fiber bundle must be maintained constant throughout the process;
- (2) fiber alignment has to be ensured;
- (3) the rollers leading the fiber to the mandrel and infiltration rollers must roll constantly and equally for homogeneous slurry infiltration;
- (4) the distance between fiber bundles after lay-up must be adjusted to fiber type, slurry system and tool geometry to avoid fiber gap or overlapping.

Filament winding machines are often equipped with a computer-aided positioning sequencer. A fully automated robot assisted with 6 + 2-axis winding machine is shown in Fig. 6.

Three-dimensional structures can be manufactured by expanding 2D preforming techniques via the stitching process (Fig. 7). The process enables high flexibility of fiber volume ratio, arrangement, insertion, and loop formation. Additionally, different fiber types can be used, albeit often carbon fibers are used. Loop formation is of particular influence on CMCs properties such as



Fig. 7 Robot assisted stitching machine for CMC preforming available at Airbus Group Innovations. Image provided by Airbus.

interlaminar or tensile strength. Furthermore, the use of this process influences the infiltration behavior since additional channels for matrix incorporation are obtained.

Matrix Infiltration Methods

The composite matrix, as well as the fibers used are very important when determining the type and properties of the composite. The matrix has a fundamental function as load distributor via internal friction mechanisms between fiber and matrix. Likewise, it enables the quasi-plastic and the damage-tolerant behavior of the composite. The fabrication method used to bring the matrix together with the fibers influences the final material properties, since the infiltration degree and the ceramic yield varies with the infiltration route used.

The processing routes for matrix infiltration can be divided into polymer infiltration pyrolysis (PIP), chemical vapor infiltration (CVI), liquid silicon infiltration (LSI), and ceramic slurry infiltration (CSI). These processes as well as their advantages and disadvantages are described in this section.

Polymer infiltration pyrolysis (PIP)

The polymer infiltration and pyrolysis (PIP) method comprises the infiltration of a low viscosity polymer into the fiber structure, followed by pyrolysis. Under pyrolysis, the polymer precursor is heated under inert atmosphere and transformed into a ceramic due to its decomposition.

The infiltration of the fiber with the polymer precursor can be done either by resin transfer molding (RTM) or via the filament winding technique. In the RTM process, the fiber preform is placed into a mold with the form of the component. Once the mold is closed, the polymer is injected into the cavity. The infiltration process is driven by capillary forces and is therefore commonly conducted at normal pressure, although it may also be vacuum- or pressure-assisted. When the filament winding technique is used, one layer of fibers in UD direction (prepreg) can be manufactured. The final material can be obtained by cutting the prepreg with the desired geometry. The prepregs are then laminated by stacking them in the desired fiber architecture (Fig. 8).

After infiltration of the fiber preform via RTM or fiber filaments via filament winding, the material is submitted to thermal treatment, during which polymer cross-linking takes place. Alternatively, cross-linking can also be initiated by radiation (either γ -rays or electronic beam). Laminated prepregs are cured under vacuum in an autoclave; cross-linking temperatures normally vary between 100°C and 200°C under pressures from 5 to 20 bars. For cross-linking in the RTM process, similar temperatures are used, although lower pressures are applied depending on the mold (Koch *et al.*, 2008; Schmidt *et al.*, 2008).

Subsequently, the material is pyrolyzed under inert atmosphere for decomposition of the organic based polymer at temperatures between 800°C to 1300°C. Volatile products such as CO, H₂, CO₂, CH₂, and H₂O are released as a result of pyrolysis, forming a porous structure in the emerging ceramic matrix. The ceramic yield is determined by the composite weight loss. The density of the formed porous ceramic can be further increased by subsequent re-infiltration cycles. The number of necessary infiltrations to reduce porosity and increase density can be reduced when ceramic fillers are added to the matrix composition.

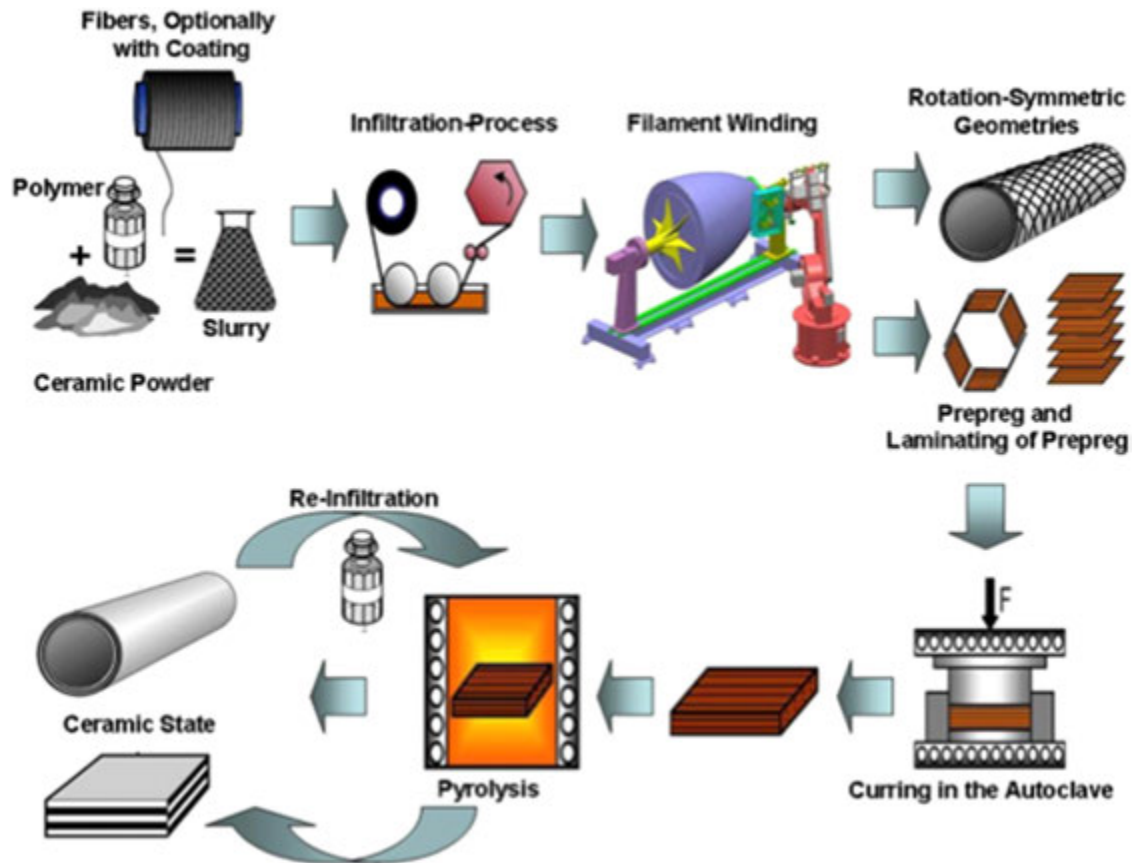


Fig. 8 Process steps of the PIP route for the fabrication of CMC. Image provided by Airbus.

This process offers several advantages, such as prevention of fiber damage due to low processing temperatures, good control of the matrix composition and the microstructure, and fabrication of near-net-shape parts and matrices of various compositions (silicon carbide, silicon nitride, silicon carbonitride). On the other hand, the process has relatively high production costs and time, due to the multiple re-infiltration pyrolysis cycles applied. Furthermore, residual silicon is found in the matrix after pyrolysis.

Chemical vapor infiltration (CVI)

Chemical vapor infiltration (CVI) is a process in which reactant gases diffuse into a heated fibrous preform and react to a solid phase on the surface of the fiber. The infiltration of the gaseous precursor into the reinforcing fiber structure (preform) is driven either by diffusion or by an imposed external pressure. Deposition fills the space between the fibers, forming a composite material in which the matrix is the deposited material and the dispersed phase is the fiber preform (Fig. 9). Chemical vapor infiltration is similar to chemical vapor deposition (CVD), by which a deposit is formed when the reactant gases react on the outer surface of the substrate.

Modified CVI processes have been developed with the aim of reducing the time needed for infiltration and to achieve progress in near-net shaping and tailoring the matrices and interphases. These modified processes include radio- or microwave-assisted CVI, pressure-pulsed CVI, forced-flow CVI, and rapid CVI.

The CVI process offers advantages such as low fiber damage – due to relatively low infiltration temperatures –, fabrication of matrices of high purity, generation of low residual stresses due to low infiltration temperatures, enhanced mechanical properties (strength, elongation, toughness), good thermal shock resistance and possibility of fabrication of matrices with various compositions (SiC, C, Si₃N₄, BN, B₄C, ZrC, etc.). Nevertheless, due to the slow processing rates, very long process times have to be stated (may continue up to several weeks depending on the material thickness) and the process involves high initial capital and production costs.

Liquid silicon infiltration (LSI)

In this process a green body is initially made by infiltrating high-carbon precursors into a fiber preform. Using roving infiltration and subsequent winding techniques or CFRP methods such as RTM, it enables near-net shaping. After precursor curing, the

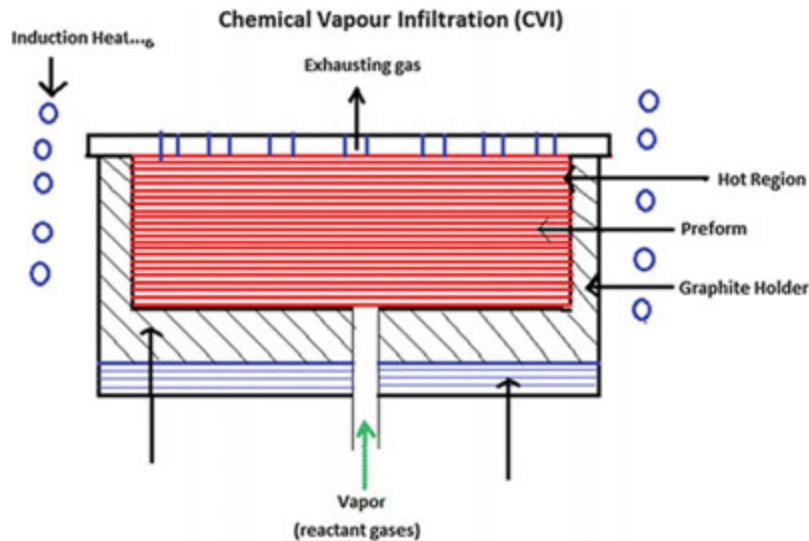


Fig. 9 Illustration of a chemical vapor infiltration (CVI) reactor. Reprinted from Sharma, R., Ravikumar, N.L., Dasgupta, K., Chakravarty, J.K., Kar, K.K., 2017. Advanced carbon–carbon composites: Processing properties and applications. In: Kar, K.K. (Ed.), *Composite Materials: Processing, Applications, Characterizations*. Berlin, Heidelberg: Springer, pp. 315–367, with permission from Springer Nature.

material is pyrolyzed under nitrogen atmosphere or vacuum at temperatures between 800°C and 1200°C. During the process, volatile products are released and a porous carbon structure is formed.

Subsequently, the preform is infiltrated with molten silicon or silicon alloys. Molten silicon is driven by capillary forces into the porous structure. The melt reacts with carbon, forming silicon carbide according to the reaction: $\text{Si (liquid)} + \text{C (solid)} \rightarrow \text{SiC (solid)}$. SiC produced by this reaction fills the preform pores and forms the ceramic matrix.

In contrast to the composites fabricated by PIP and CVI, ceramic matrices formed by liquid silicon infiltration are fully dense (have zero or very low residual porosity). Additionally, it is a low cost technique with short production times, which allows the fabrication of complex and near-net-shape composites with improved thermal and electrical conductivity.

Ceramic slurry infiltration (CSI)

In the ceramic slurry infiltration (CSI) technique, a liquid slurry is used to infiltrate the fiber preform or fiber roving via filament winding. Capillary forces drive the infiltration process and water or sol-gel based slurries may be used.

Water based slurries contain dispersed ceramic fillers, binder, dispersing and/or wetting agents. The most usual ceramic fillers are alumina (Al_2O_3), silica (SiO_2), glass, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), silicon carbide (SiC) or silicon nitride (Si_3N_4). These slurries are, after infiltration within the fibers, consolidated via hot pressing. Hot pressing is performed at high temperature and increased pressure, which enhances the intrusion of the ceramic material into the fiber structure. The particles consolidate, resulting in low-porosity, densified composites with good mechanical properties. The reinforcing fibers may be, however, damaged by the high pressure applied in the hot pressing stage. In addition, hot pressing requires relatively expensive equipment and allows the fabrication of only small and simple parts.

Alternatively, sol-gel based suspensions can be used for the fabrication of CMC. Colloidal suspensions containing fine ceramic particles of up to 100 nm are dispersed in water or organic solvents. Ceramic fillers such as alumina and mullite may be added to the suspension in order to increase the material strength and reduce porosity and shrinkage. The suspension is infiltrated into the fibers using, for example, the filament winding technique and consolidated via gelation.

At elevated temperatures, sols containing organometallic compounds (e.g., alkoxides) undergo cross-linking (polymerization) by either the polycondensation or hydrolysis mechanism. Polymerization converts sol into gel and the gels may be transformed into ceramics at relatively low sintering temperatures, which reduces the probability of fiber damage. After gelation, the material must be dried for removal of water or the organic component. Re-infiltration with sol followed by drying and sintering may be conducted if higher densification of the material is desired.

The gelation or consolidation of the ceramic suspension takes place, nevertheless, not only by elevating temperature but also, for example, by application of pressure, pH change or submission of the material to temperatures below zero degree, i.e., the freeze gelation technique.

State-of-the-Art in Ceramic Matrix Composites Development

In the early 1990, the manufacture of ceramic matrix composites using the freeze gelation technology was investigated. Early studies report the use of colloidal suspensions for the preparation of monolithic ceramics by a freeze casting route where different

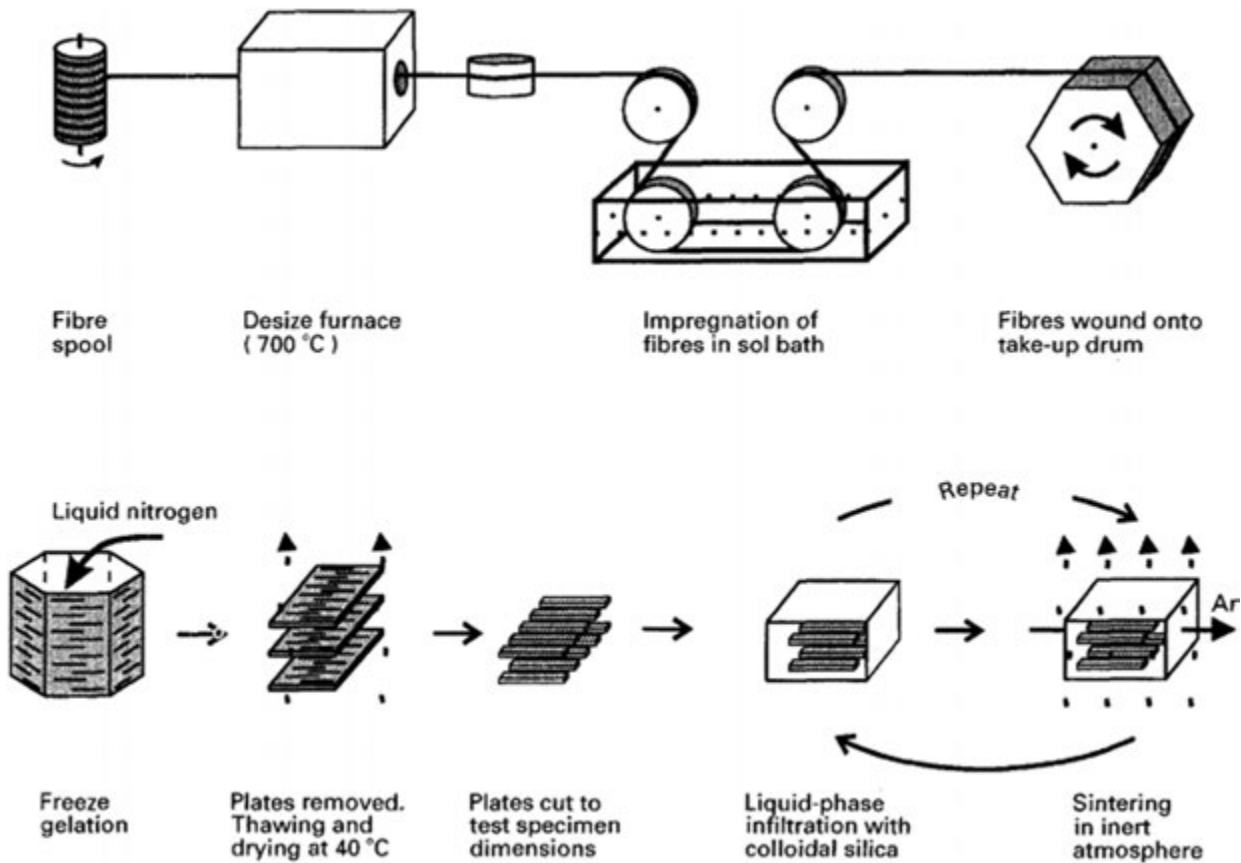


Fig. 10 Filament winding route used to fabricate samples with sol-gel matrix system at the University of Bath. Reprinted from Chant, J.M., Bleay, S.M., Harris, B., *et al.*, 1995. Mechanical properties and microstructures of sol-gel derived ceramic-matrix composites. *J. Mater. Sci.* 30, 2769–2784, with permission from Springer Nature.

sols with different particle sizes (without addition of ceramic filler) were investigated (Statham *et al.*, 1998; Laurie *et al.*, 1992). Freeze gelation was then used to manufacture ceramic matrix composites. Primarily, studies involved the use of different fibers such as glass, carbon, Si-based and Al_2O_3 fibers that were infiltrated via different techniques, such as filament winding, resin transfer molding, hot pressing, casting or injection molding.

Moreover, extensive work in analyzing the freeze gelation process parameters and their influence on the final properties of the composite were conducted, leading to a substantial growth in the knowledge on the gelation of colloidal sols, on the influence of amount and particle size of the fillers, as well as on the sintering and infiltration process steps (Russell-Floyd *et al.*, 1993a,b).

Matrices were first developed using colloidal silica sol systems with average particle sizes of 125 nm with dried amorphous silica and glass fillers and/or colloidal silica sol with average particle size of 25 nm with dried amorphous silica and quartz fillers. Suspensions were used to impregnate carbon fiber T300 via filament winding and to produce unidirectional composites (Fig. 10). After winding in a hexagonal mandrel, liquid nitrogen was poured into the mandrel to cause freeze gelation of the matrix. After thawing to room temperature and drying at 40 °C, test specimens were cut and infiltrated under pressure with colloidal silica with particle size of approximately 7 nm and sintered at 600 °C in argon. Samples were infiltrated seven times and sintered after each time at temperatures of 600 °C, 750 °C, 900 °C, 1100 °C, and 1400 °C (Chant *et al.*, 1995).

Unidirectional composites made with amorphous silica and glass ceramic filler showed bending strengths of approximately 150 MPa. In the composites made with amorphous silica and quartz filler, bending strengths of up to 200 MPa were observed (Chant *et al.*, 1995).

Composites using Nextel™ 440 oxide fibers have also been reported (Twitty *et al.*, 1995). The ceramic matrix was manufactured with an aqueous sol (50 wt% SiO_2 , 50 wt% water) and 61 wt% of ZrO_2 as filler. Unidirectional prepreps were produced via filament winding. These sheets were wet-pressed between stainless steel plates to produce $100 \times 100 \times 5 \text{ mm}^3$ plates. The pressed plates were frozen with liquid nitrogen. After drying, the plates were re-infiltrated three times with Syton D30 silica sol, dried between infiltration steps and then sintered at 950 °C for one hour. The sintered plates were infiltrated twice more. Finally, the samples were infiltrated three times and sintered at 500 °C for 90 min. Final composite fiber volume was between 23 vol% and 28 vol% and porosity of 30 vol%. Table 1 summarizes the properties of the composites manufactured with Nextel™ 440 and silica-zirconia matrix. No information on these materials interlaminar properties is given in literature.

Table 1 Mechanical properties of unidirectional composites manufactured with Nextel™ 440 and silica-zirconia matrix at the University of Bath

Batch	Fiber content (vol%)	Flexural modulus (GPa)	Flexural strength (MPa)	Work of fracture (Jm^{-2})
1	26 ± 1	31 ± 6	79 ± 18	477 ± 155
2	23 ± 1	36 ± 2	84 ± 14	502 ± 111
3	28 ± 1	41 ± 4	83 ± 13	871 ± 256

Note: Adapted from Twitty, A., Russell-Floyd, R.S., Cooke, R.G., Harris, B., 1995. Thermal shock resistance of nextel/silica–zirconia ceramic-matrix composites manufactured by freeze-gelation. *J. Eur. Ceram. Soc.* 15, 455–461, with permission from Elsevier.

Conclusions

Different combinations of matrix, fiber, fiber coating, fiber infiltration technique, and consolidation method can be used to manufacture ceramic composites. Each combination leads consequently to differences in the mechanical performance of the material. The use of an automated technique such as filament winding confers to the composite reproducibility, homogenous infiltration of ceramic fibers and short manufacturing times, reflecting in better mechanical performance of the composite manufactured.

Colloidal processing of ceramics can be used in combination with different gelation methods. The freeze gelation process is highlighted due to its versatility, simplicity and at the same time allows a cost-efficient way to manufacture ceramic bodies. The suspension is, in this case, consolidated by freezing at temperatures below 0°C. Moreover, due to rapid freezing of stable suspensions, porosity is homogeneously distributed in the matrix enhancing the material performance.

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Porous Oxide Ceramic Matrix Composites – Properties, Manufacturing, and Applications

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Introduction

Oxide CMC with porous matrices belong to the “ceramic matrix composites” (CMC) class of materials a term mostly assigned to fiber-reinforced ceramics, i.e., ceramic matrices are reinforced by ceramic fibers. In contrast to monolithic ceramics, CMC exhibit a, “quasi-ductile” fracture behavior, resulting in linear-elastic deformation until non-brittle failure upon mechanical overload. Unlike classical composite materials such as fiber-reinforced plastics (GFRP, CFRP) where matrices and reinforcing ceramic fibers exhibit strongly differing mechanical properties such as (tensile) strength, modulus, CMC are built from highly similar materials, i.e., ceramic fibers and ceramic matrices with similar materials properties such as modulus, strength, etc. The non-brittle, frequently referred to as “damage-tolerant” fracture behavior of CMC is enabled by progressive debonding of reinforcing ceramic fibers and disintegration of the ceramic matrix under mechanical load and governed by micromechanical effects such as microcracking, crack-deflection, -bridging, fiber pull-out and fiber rupture. Generally speaking, CMC rely on a sufficiently weak bonding between ceramic matrix and ceramic fibers. Too strong bonding between ceramic matrix and ceramic fibers can be avoided by introducing a weak interphase between fibers and matrices, which can be realized for example by a porous or “cleavable” fiber coating. Such CMC are commonly referred to as “weak interface composites”. The discussion of this class of CMC materials, however, is beyond the scope of this article and the reader is encouraged to refer to relevant review literature. “Sufficiently weak” CMC without any additional fiber-matrix interphases can also be realized by means of highly porous matrices. Such oxide CMCs with porous matrices have been reported first the mid 1990’s by the University of California, Santa Barbara (USCB; [Lange et al., 1995, 2000; Levi et al., 1998](#)). The major constituents of state-of-the-art oxide CMC are alumina (Al_2O_3) and silica (SiO_2), boria (B_2O_3) is frequently used as minor component of commercially available oxide fibers. CMC-relevant phases are consequently $\alpha\text{-Al}_2\text{O}_3$ (Corundum), $\text{Al}_6\text{Si}_2\text{O}_{13}$ (Mullite) and aluminosilicates or boro-aluminosilicates. Whereas Al_2O_3 - and mullite-based CMC designed for applications at temperatures of 1000°C and beyond are fully crystalline, boria-containing CMC hold significant amounts of glassy phases which are not capable to carry mechanical loads at high temperatures beyond 800°C. The present article is focusing on boria-free, fully crystalline oxide CMC in the following. Such high-performance, porous oxide CMC display a unique combination of physico-chemical properties which makes them interesting structural materials for high-temperature structural applications in various fields of application in aeronautics, space, and industrial thermal process technology.

Properties of Porous Oxide CMC

A characteristic feature of porous of Oxide CMC are highly porous matrices typically consisting of standard engineering ceramics such highly pure alumina or aluminum silicates such as mullite. With a typical fiber volume content between 30 and 50 vol%, the overall porosity of oxide CMC are generally in a range of 15–35 vol%. Along with typical oxide fiber volume contents between 30 and 50 vol%, resulting total porosities of CMC are in a range of 15–35 vol%. A high porosity inevitably results in relative low matrix strength and toughness. Consequently, this material concept has been commonly referred to as “Weak Matrix Composite” in the literature. [Fig. 1](#) shows the typical microstructure of such kind of materials.

The bonding between a particulate matrix and reinforcing fibers is evidently punctual and governed by the local matrix porosity. Therefore, also the fiber-matrix bonding can be considered also relatively weak, allowing for energy dissipation at the fiber/matrix interface and limiting stress transfer into fibers. Consequently, a substantial proportion of fracture energy is dissipated by microcracking and disintegration of the porous, low toughness ceramic matrices prior to widespread fiber fracture. This results in the typical damage-tolerant, “quasi-ductile” fracture behavior of porous oxide CMC. The stress-strain curve plotted in [Fig. 2](#) represents the typical fracture behavior of a porous oxide CMC. Initially, the material deformation is linear-elastic, followed by stepwise progressing failure, indicating multiple delamination events. Compared to similar unreinforced (monolithic) ceramic materials which typically display a higher elastic modulus but significantly lower strain and brittle failure, oxide CMC show considerably higher pre-failure deformation and can carry a substantial residual load after initial fracture, a behavior which is often referred to as “pseudo-plastic” or “quasi-ductile”.

Similar to all continuous fiber-reinforced materials, porous oxide CMC are highly anisotropic. Mechanical properties are strongly dependent on fiber-architecture as well as load direction. As a general rule, mechanical stresses parallel to the long fiber-axes are much less critical than “off-axis” stresses, i.e., where mechanical loads must be carried predominantly by the porous matrix. Strength differences of a factor of four are not unusual. The fact that porous oxide CMC are typically laminar materials implies that matrix-dominated, interlaminar strength is relatively low and shear failure is a serious issue. Detailed analyses of the mechanical behavior of porous CMC have been reported shortly after these materials gained significant attention in research & development ([Tu et al., 1996; Heathcote et al., 1999; Levi et al., 1999; Zok and Levi, 2001](#)). Comprehensive characterizations of

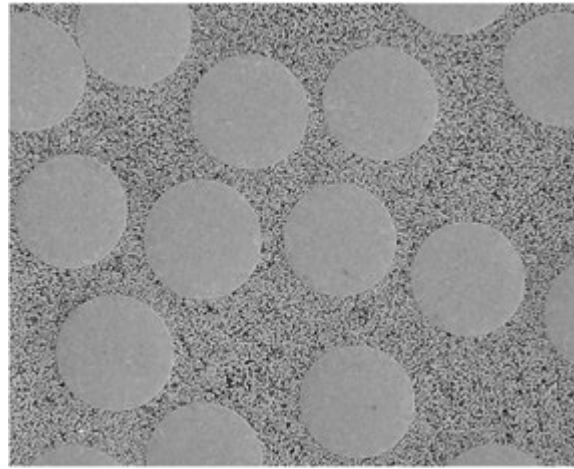


Fig. 1 Typical microstructure of porous oxide CMC featuring dense polycrystalline oxide fibers embedded in a small-grained porous oxide matrix. Source: DLR.

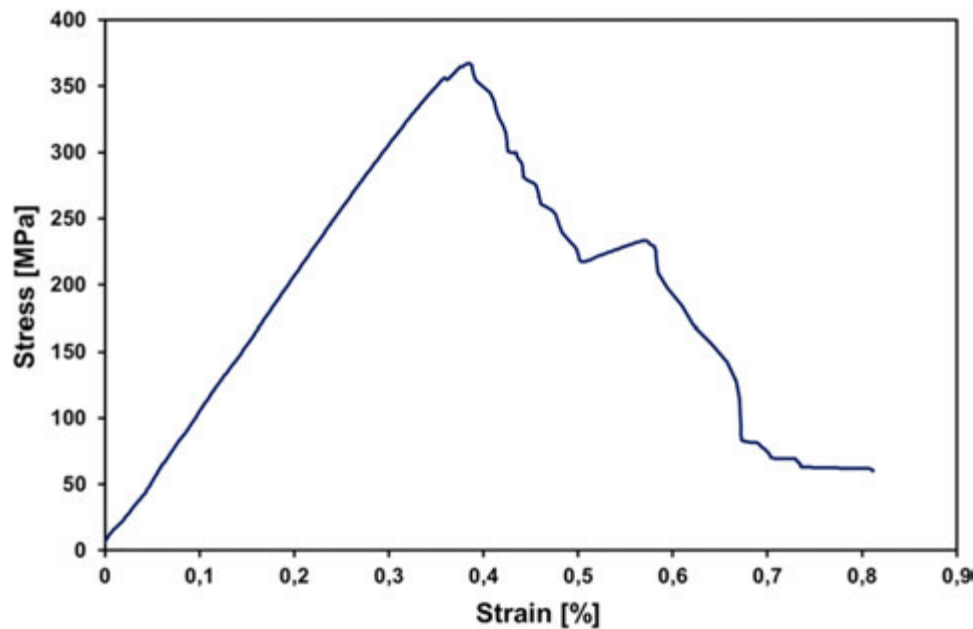


Fig. 2 Typical fracture of porous oxide CMC with initial linear-elastic deformation followed by progressive failure. Source: DLR.

various oxide CMC materials can be found in [Volkman et al. \(2015\)](#). General information on the mechanical properties of CMC can be found in [Koch et al. \(2008\)](#) and in other review work ([Zok, 2006](#); [Keller et al., 2014](#); [Tushev and Almeida, 2018](#)).

In order to optimize CMC mechanical properties, the “weak” ceramic matrices must be reinforced with “strong” high-performance oxide fibers ([Bunsell and Berger, 2000](#)). State-of-the art continuous oxide fibers are polycrystalline; the diameter of individual filaments is mostly between 10 and 12 μm . The mechanical strength of polycrystalline oxide fibers is typically correlated with their grain sizes, where small, in particular nanometer sized grains are generally favorable. As a consequence, any mechanism resulting in fiber grain growth is considered detrimental to CMC mechanical properties ([Schmücker et al., 2012](#)). The dominant trigger for grain growth in oxide fibers is thermally activated diffusion of species which limits not just the tolerable peak operating temperatures in long-term applications (hundreds to thousands of hours) but also the maximum sintering temperature during CMC processing. Therefore, high-end oxide fibers have specifically designed microstructures which shall mitigate excessive grain growth ([Wilson and Visser, 2001](#)). The commercially most employed pure alumina fibers (Nextel™ 610, 3M, St. Paul, MN, USA) are doped with few tenths of a percent iron oxide and silica, acting as nucleation agent and grain boundary stabilizer, respectively: whereas iron oxide enhances nucleation of many small alumina grains silica is accumulating at grain boundaries and slows down intergranular diffusion and subsequent grain growth of alumina. An alternative concept for reducing oxide fiber grain growth is a

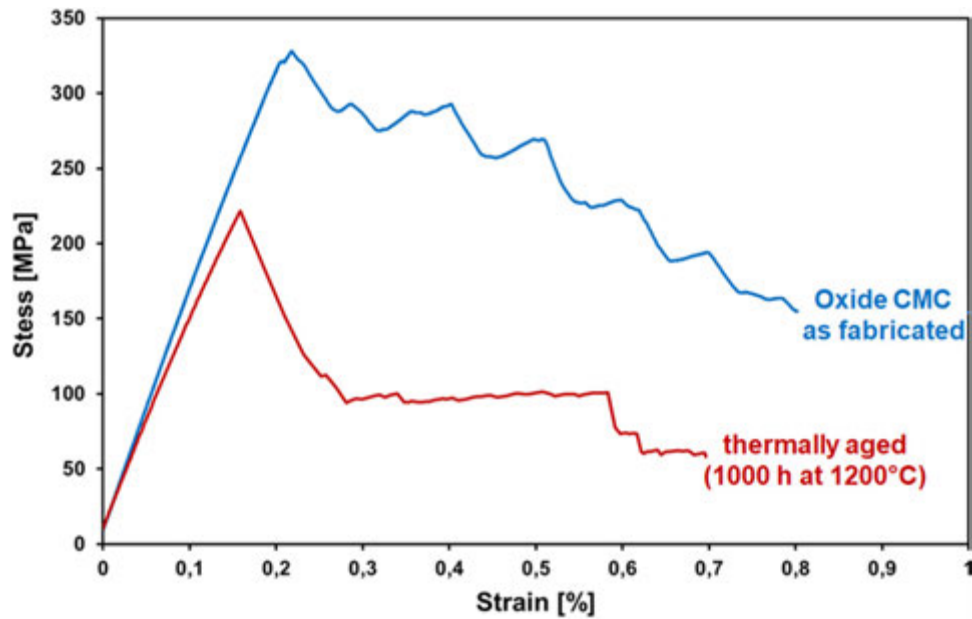


Fig. 3 Solar furnace testing of Al_2O_3 materials: whereas the CMC is melting at the hot focal point, a monolithic reference is shattered instantaneously. *Source:* DLR.

specifically designed two-phase microstructure: the chemical composition of 3M's Nextel™ 720 fibers (85% Al_2O_3 + 15% SiO_2) results in an approximately 50 vol% Al_2O_3 –50 vol% Mullite assemblage where both phases mutually mitigate growth and coalescence of grains. Typical tolerable short-term peak temperatures are 1300°C for alumina fibers and 1400°C for mullite/alumina fibers, respectively. The onset temperatures for long-term thermal grain growth, however, are at least 100 K lower. The growing demand for alternative sources for high-performance oxide fibers triggered a variety of research and development activities. Pure mullite fibers, promising enhanced creep resistance and suitable mechanical strength, have been developed up to a semi-commercial level by the Deutsche Institute for Textiles and Fibers (DTIF, Denkendorf, Germany) and the name CeraFib / OxCeFi (Clauss and Schawaller, 2006; Almeida *et al.*, 2015). Other efforts have been made to enhance fiber properties by alternative formulations such as zirconia-alumina, yttrium aluminum garnet, etc. (see e.g., Krüger *et al.*, 2002; Pfeifer *et al.*, 2016); however, none of them have yet resulted in commercially available fibers having superior properties than state-of-the-art Nextel™ fiber variants (Fig. 3).

The key features of porous oxide CMC, i.e., relative weak matrices, weak fiber-matrix interfaces, and strong fibers, however, suffer from thermally activated effects: sintering produces stronger matrices as well as interfaces; grain growth results in significantly reduced fiber strength. Thermally induced fiber-matrix interactions play also key role for the stability: sintering of matrix particles to the fiber surface results in undesirable “strong” interfaces (Schmücker *et al.*, 2000). A special effect related to the SiO_2 fiber doping has been observed in $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ CMC – outdiffusion of SiO_2 into the Al_2O_3 matrix can trigger excessive growth in fibers and across the fiber-matrix interface (Schmücker and Mechnich, 2008). As a consequence, porous oxide CMC are highly susceptible to “thermal aging” (Carelli *et al.*, 2002). Fig. 4 displays a comparison of a filament-wound CMC before and after isothermal aging for 1000 h at 1200°C. Both bending strength and deformation limit deteriorate significantly – the aged material shows a much higher “brittleness”. Environmental effects such as high moisture can significantly worsen the aging problem (see e.g., Ruggles-Wrenn, 2014).

A second major detrimental mechanism affecting oxide CMC is creep deformation, i.e., material flow at high temperature under applied stress. Oxide materials are generally prone to creep deformation due their more ionic bonding characteristics and diffusivity as compared to more covalently bonded non-oxide materials. With regard to creep deformation, grain size effects become important in oxide CMC as well. In particular the small grain sizes of oxide fibers makes them susceptible to grain boundary diffusion dominated creep deformation (so-called “Coble creep”). Fiber creep deformation can also be minimized by use of selected materials and specific microstructural design. The combination of the a priori more creep resistant phase Mullite and their “interpenetrating” mullite/alumina microstructure makes 3M's Nextel 720 fibers approximately four orders of magnitude more creep resistant than similar Nextel 610 Al_2O_3 fibers. Consequently, CMC fabricated from Nextel 720 fibers and mullite matrices display much less creep deformation than their $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ counterparts (Fig. 5). Many studies have been performed to access the creep of porous oxide CMC, see e.g., Ruggles-Wrenn *et al.* (2008), Hackemann *et al.* (2010) and aforementioned reviews.

In general, there is a contrary grain size effect on fiber strength and creep resistance. Therefore, the CMC architecture must be carefully adapted to the thermo-mechanical environment of the envisaged application: although the strength of mullite-based fibers and CMC is a priori lower, they may outperform Al_2O_3 -based fibers and CMC in long-term structural applications at

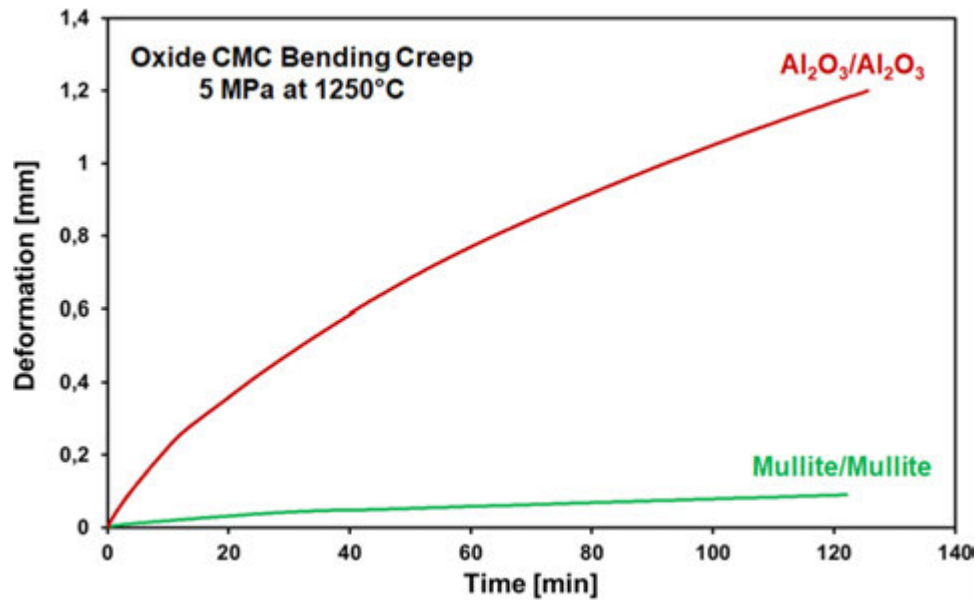


Fig. 4 Effect of thermal aging on the fracture behavior of porous oxide CMC: strength as well as deformation capability suffer from thermally driven effects such as sintering and grain growth. *Source:* DLR.

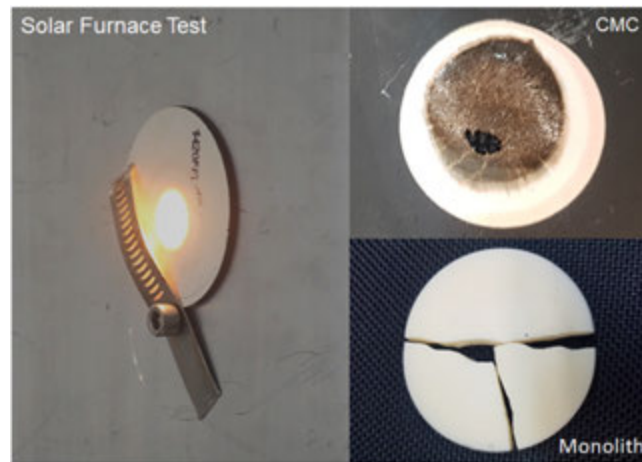


Fig. 5 Creep deformation of porous oxide CMC proving the superior performance of Mullite-based materials. *Source:* DLR.

operation temperatures beyond 1000°C. It must be emphasized, however, that creep deformation is a major limitation for high-temperature application of any kind of oxide CMC.

In addition to their characteristic thermo-mechanical behavior, porous oxide CMC display further distinct properties. Owing to their relative high porosities and oxide constituents, their thermal conductivities are comparatively low, typical values range from 4 to 2 W/mK for alumina-based materials, and meet the demand for materials to be used for high-temperature thermal insulation. The thermal expansion of oxide CMC is evidently similar to their constituents Al₂O₃ and mullite, i.e., CTE values between 8 and 5 ppm/K are typical. Moreover, critical, i.e., discontinuous phase transformations do not occur in alumina and mullite up to their respective melting temperatures of about 2050°C and 1830°C. However, due to their relatively low thermal conductivities application of porous oxide CMC under very high thermal gradients and transients may become critical since laminar thermal stresses may exceed material limits. This is considered particularly critical when porous oxide CMC tubes are applied as hot gas leading components, for example in gas turbines. Similar to many oxide ceramics, porous oxide CMC are non-conducting, dielectric materials which are interesting for special applications where transparency for electromagnetic fields is important. Inherent low density, oxidation resistance and overall high chemical inertness add to the unique combination of properties which qualifies porous oxide CMC as substitute for monolithic oxide ceramics as well as lightweight, high-temperature structural materials with high durability, enabling new applications of oxide ceramic materials in harsh environments. Again, matrix-dominated energy dissipation and limited stress transfer come into play: porous oxide CMC perform very well under point loads:

a nail can literally be “hammered” into porous oxide CMC; resulting only in local damage without catastrophic failure by fragmentation. A similar behavior is observed if porous oxide CMC are exposed to focused thermal radiation such as concentrated sunlight or LASER beams. High radial thermal gradients and transients produce rather melting at the hot spot than fragmentation of the CMC body.

Fig. 3 shows a test performed in a solar furnace at the DLR Institute of Solar Research. Whereas the $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ CMC disc has “only” been melted at the about 10 mm wide focal point, a reference sample of monolithic Al_2O_3 has been shattered instantaneously. This resistance versus “thermal shock” is considered a unique feature and makes oxide CMC very interesting materials for demanding applications such as concentrated solar power.

Manufacturing of Porous Oxide CMC

Standard fabrication methods for composite materials based upon continuous fibers are also employed for porous oxide CMC. Commercial oxide fibers are available in different specifications, typical tow dimensions are ranging from 1500 and 20,000 denier, where tows hold from 400 up to more than 5000 individual filaments. An important aspect for the processing of oxide fibers is their sizing, which is frequently applied by the fiber manufacturers. This sizing is employed for improved handling and textile processing of fiber tows. Frequently, organic polymers are used as fiber sizing. However, fiber sizings are detrimental for CMC processing since they impede homogenous infiltration of fiber tows by matrix precursors. Therefore, thermal removal of fiber sizings prior to infiltration steps must be considered for CMC manufacturing.

Presumably the most straightforward CMC manufacturing variant is based upon woven oxide fiber fabrics which are infiltrated with a dispersion of matrix particles, the so called “matrix slurry”. Examples can be found in [Levi et al. \(1998, 1999\)](#), [Zawada et al. \(2003\)](#), or [Simon \(2005\)](#). Matrix slurries are generally optimized for infiltration with focus on particle load and size distribution, and typically consist of nanoscaled Al_2O_3 and/or Mullite powders, in some cases also ZrO_2 powders as additional fillers have been employed. Water is preferably used as non-toxic dispersion medium, however liquid, sometimes non-aqueous binders such as colloidal SiO_2 have been employed. CMC shaping is performed by cutting the resulting “pre-pregs”, laminating, drying, and final thermal consolidation (“sintering”), which is typically performed in ambient air at temperatures between 1200 and 1300°C (see e.g., [Shi et al., 2018](#)). Alternatively, the CMC shaping step can be improved by means of vacuum bagging and pressure-assisted consolidation in an autoclave. A much more sophisticated manufacturing route is based upon oxide fiber preforms which are fabricated by means of textile technologies such as weaving, braiding, knitting and sewing. The intrinsic brittleness of oxide fibers and their limited bending and shear strength, however, limits the forming capability substantially. In particular it is extremely difficult to arrange oxide fibers into preforms with low bending radii. Moreover, oxide fibers are prone to fracture during handling of tows and woven fabrics. Therefore, standard textile technologies must be adapted to the mechanical vulnerability of oxide fibers. Finally, fiber preforms are infiltrated by a matrix precursor, either as specific slurry or solution with process-adapted particle load and size distribution. Infiltration as well as consolidation can also be assisted by vacuum and/or pressure, similar to common fabrication methods for composites such as resin transfer molding (RTM). Final thermal treatments are performed as described above.

In the filament winding technology demonstrated at DLR ([Kanka and Schneider, 2000](#)) continuous oxide fiber tows are employed instead of woven textiles or other fiber preforms. In a first step fiber tows are drawn through a tube furnace in order to burn off the organic fiber sizing. The de-sized fiber tow is cooled down and subsequently infiltrated, again with matrix slurries optimized for this specific process. Infiltrated fiber tows are wound up on a rotating mandrel, dried, and removed as entire tubular body from the mandrel. Alternatively, the as-wound CMC tube is cut and removed from the mandrel shortly after winding, i.e., still being in the “wet” state. The resulting CMC tape can be re-shaped, in particular flattened out before further processing steps. A vacuum- or pressure assisted post-consolidation of as wound, wet CMC tapes or bodies is basically possible. The final sintering step is performed similar to previously described processing methods. The filament winding of CMC comprises a lot of process parameters which directly translate to highly variable fiber architectures, which can be considered as “mesostructure” ([Schmücker et al., 2003](#)). Depending on the mandrel radius, the mandrel rotating speed, and the fiber tow guide speed, many varying winding patterns can be realized. A general feature of all winding processes are distinct areas where fiber tows are crossing and frequently an enrichment of the ceramic matrices is observed. The special process features of filament winding can be exploited to adapt the fiber architecture of CMC tubes to expected loads; at least to a certain extent. On the other hand, the re-shaping of tubular bodies to flat CMC “sheets” inevitably leads to some disarrangement of the as-wound fiber architecture, which has to be considered during designing of non-tubular components. Generally, filament winding is considered the preferred technique for manufacturing of tubular oxide CMC components.

Application and Industrialization of Porous Oxide CMC

There are many potential applications where CMC offer advantages over other oxide ceramic materials. First and foremost, CMC come into play in high-temperature applications where serious safety concerns prevent the application of monolithic oxide ceramics, i.e., where brittle fracture behavior can lead to catastrophic failure. Consequently, researchers and developers around the world set their focus on hot-gas exposed components of gas turbine engines as first target applications for porous oxide CMC.

An outer, annular combustor liner was manufactured by the U.S. company ATK-COI Inc. and successfully tested in a Solar Turbine stationary gas turbine; a cumulated operation time of more than 30,000 h was achieved. R&D activities at the German Aerospace Center (DLR) involved manufacturing of can-type combustor liners from DLR's WHIPOX-CMC (wound highly porous oxide) and subsequent rig testing (Fig. 6).

Growing experience and knowledge on the thermo-mechanical limits of porous oxide CMC, however, shifted the focus from the combustor to “downstream” turbine applications, i.e. areas where potential components face a much smaller thermal load. A German consortium including the company Schunk Materials, and DLR evaluated the application of Schunk's DURAFOX material as porous oxide CMC inter-turbine duct, a component connecting the high- and low-pressure turbine. The first real commercial industrial application of porous oxide CMC in aeronautics has been established by the U.S. companies General Electric (GE Aviation), Composite Horizons LLC (CHI), and Axiom Materials Inc. GE's “Passport” turbine engine is equipped with an oxide CMC mixer providing better mixing of very hot exhaust gas from the core engine and cool bypass air at reduced weight and improved vibration stability compared to conventional exhaust mixers made of titanium. The companies 3M, CHI, and Axiom investigated promising pathways to further diminish costs for industrial CMC manufacturing by means of weaving fiber fabrics from tows with higher denier count (Lincoln *et al.*, 2017).

Space transportation and hypersonic flight are further fields where oxide CMC have been successfully applied. In various missions, porous oxide CMC have been employed as light-weight, heat-resistant materials for thermal protection systems. The nose cap of DLR's hypersonic re-entry vehicle SHEFEX (sharp edge flight experiment) was equipped with various WHIPOX heat protection shingles as well as an EM-transparent cover for the antenna, allowing for data transmission at elevated temperatures. The specific combination of EM transparency, heat resistance and good thermal insulation were also the reason for employing a spherical WHIPOX protection capsule for the data recorder/transmitter “Break-Up Camera” monitoring the re-entry and disintegration of ESA's space vehicle “ATV Jules Verne” (Fig. 7).

The unique properties of porous oxide CMC have also drawn attention to standard applications in industrial thermal processing. Among the first use-cases were long-lasting nozzles for natural gas burners which were demonstrated and commercialized by the German company Pritzkow Spezialkeramik. WPX-Faserkeramik GmbH, a spin-off company from DLR, has commercialized the WHIPOX material targeting industrial processing of metals such as annealing, hardening, or soldering. Transport racks, charge carriers, or separators made of lightweight, grid- or mesh-type oxide CMC exhibit superior durability in most atmospheres and



Fig. 6 Prototype micro-turbine combustor liner fabricated by filament winding. *Source:* DLR.



Fig. 7 Thermal protection capsule for space application fabricated by filament winding. *Source:* DLR.

promise higher energy efficiency due to better thermal resistance and heat capacity. The chemically stable oxide material avoids any contamination of metal parts by carbon or other metals. Further applications of porous oxide CMC are being evaluated in metallurgy. The company Schunk has demonstrated promising low wetting of DURAFOX-type CMC by Aluminum melts. Due to their unique combination of industry-relevant properties it is anticipated that many other fields of applications for porous oxide CMC will emerge in the future.

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Fabrication Methods and Characterization Techniques for Porous Ceramic Materials

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Introduction

Several decades down the line, the utilization of ceramic materials as household hardware, industrial use and structural applications have received tremendous acceptance amidst various end users owing to their high thermal stability, chemical resistance, good wear resistance, poor conductivity, high hardness etc. This group of materials has surged the interest of researchers by delving further into advancing the development of ceramic products that can suit other specific requirements. Thus far, studies have shown the major setbacks in the use of ceramic materials for structural applications to be the brittleness and the constant evolution of pores within the microstructure which serves as fracture sites thereby deteriorating the structural integrity of this group of materials [1–4]. However, systematic control of these pores have been channeled towards the development of porous ceramic materials suitable for application in wide-ranging technologies such as filtration, thermal insulation, food processing, biomedical implants and others [5–9].

To a large extent, ample homogenous porous ceramics have been largely manufactured through the utilization of state-of-the-art processing methods [10]. Meanwhile, it has been reported that the utilization of appropriate fabrication technique promotes the proper tailoring of pore network in porous ceramic materials and in turn creates an expansion in the application areas of these materials [11]. More so, for certain application areas, it is of utmost importance to employ appropriate processing method that will establish the required tradeoff between the infused microstructure and the mechanical properties of the developed porous ceramics [12]. For instance, the development of scaffolds with infused pore network for bone tissue engineering application requires the establishment of a tradeoff between the necessary mechanical properties and the porosity level of the scaffolds [13,14]. Specific requirements are essential for their utilization as solid oxide fuel cells where open hierarchical pore structure (50–150 μm) is required for adequate diffusion of the reactants to the active reaction area [15,16].

Considering the numerous studies carried out thus far on the development of porous ceramic materials and the prevalence of these materials in broad-based and strategic industrial technologies these days, there is a pressing need for the documentation of various characterization techniques required for the evaluation of porous ceramic materials. Finally, in order to expand the versatility of porous ceramics for industrial applications, the article gives detailed information on the fabrication methods and characterization techniques for evaluating the porosity, microstructure and mechanical properties of porous ceramic materials.

Fabrication Methods for Developing Porous Ceramic Materials

Having highlighted the relationship between the fabrication techniques and the properties of porous ceramic materials, a systematic evaluation of the existing fabrication methods will thus be discussed. Despite the broad-based application areas of porous ceramic materials, it is highly recommended for industrial experts and researchers to place more concentration on determining the appropriate fabrication methods for developing porous ceramics since the resultant microstructure, mechanical and other physical properties are dependent on the fabrication technique used. The fabrication methods for the development of porous ceramic materials can be divided into four basic categories: (i) partial sintering, (ii) replica template, (iii) pore-forming agent and (iv) direct foaming.

Partial Sintering Method

Among the existing fabrication methods, the partial sintering method has been reported as the easiest method for developing porous ceramic materials with homogeneously distributed pores and durable strength [17]. As the name implies, the procedure for this method involves the utilization of partial sintering process accompanied by surface diffusion, evaporation-condensation, recrystallization or a solution-precipitation process to bond particles of powder compact [18]. Hence, the prevention of full densification leads to the emergence of porous ceramics with homogeneously distributed pore cavities. Ohji and Fukushima proposed that the formation of pores with controlled size in partially sintered porous ceramic materials is dependent on the size of the powder particles which must be two to five times larger than the required pore size [19]. The authors further highlighted increased forming pressure, high sintering temperature and elongated time interval as the parameters responsible for porosity reduction.

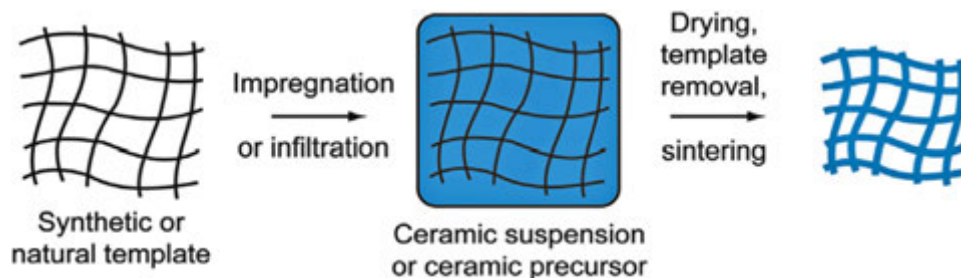


Fig. 1 Replica template method for fabricating porous ceramics. Reproduced from Hammel, E.C., Ighodaro, O.R., Okoli, O.I., 2014. Processing and properties of advanced porous ceramics: An application based review. *Ceramics International* 40 (10), 15351–15370.

In their study, Eom *et al.* reported a relationship between the elastic modulus and the neck radius to particle radius ratio wherein the resultant neck formation allows the elastic behavior to be related directly with the sintering kinetics [18]. Adopting the partial sintering method and a relatively low sintering temperature range (1550–1850°C), Tuyen *et al.* developed reaction-bonded silica nitride (RBSN) porous ceramics [20]. In the course of studying the effect of different sintering temperatures on the porosity and compressive strength of porous RBSN ceramics, the investigators observed porosity decrease and a corresponding rise in the compressive strength of the porous ceramics with increasing sintering temperature; where the samples sintered at 1550°C exhibited porosity and compressive strength of 43.2% and 141 MPa respectively while in a similar sequence, samples sintered at 1850°C exhibited 38% and 285 MPa respectively.

Replica Template Method

The replica template method has far been frequently employed by both researchers and industrial experts for the fabrication of porous ceramic systems with high porosity and hierarchical pores. The fabrication process is based on the impregnation of a typical template (porous or cellular structure) with ceramic slurry or precursor solution (see Fig. 1) [19]. With a view to developing defect-free porous ceramics, it is highly essential for the utilized template to have homogeneously dispersed open cell structures as well as adequate ductility for rapid shape recovery after usage [21]. Among the various natural and synthetic cellular materials available for fabricating the replica template, the polymeric sponge (e.g., polyurethane) has been the most utilized synthetic template since it meets the requisite properties highlighted above.

Embarking on the utilization of the replica template method, Soy *et al.* successfully developed reticulated porous SiC ceramics by utilizing polyurethane sponge for the fabrication of highly porous ceramic foam and firing up the samples at 500°C for 30 min to eject the polyurethane sponge [22]. The investigators observed the evolution of a refined microstructure owing to the high sintering (1300°C) with the presence of diminutive pores within the pore walls as a replacement for shrinkage which promotes dimension control and liquid metal infiltration. Xue and Wang developed porous SiC ceramics by infiltrating porous carbon from carbonized waste cotton linter with liquid silicon in a vacuum oven at 1550°C [23]. Meanwhile, the authors attributed the remarkable properties (porosity, bending strength and fracture toughness) exhibited by the porous SiC ceramics to the efficient control of the Si removal time. Similarly, Li *et al.* developed highly porous zirconium carbide-silicon carbide (ZrC-SiC) ceramics by employing a hybrid sol as a precursor and melamine foam as templates [24].

Pore-Forming Agent Method

Aside from the fabrication techniques highlighted in the sections above, pores can be infused into the microstructure of ceramic materials by incorporating the appropriate quantity of pore-forming agent into ceramic powder particles through a mixing process. After the homogenization process, the powder blend is pressed to produce green pellets which will be subjected to a heat treatment process for the ejection and decomposition of the pore-forming agent. Fig. 2 presents the schematic diagram of the pore-forming agent for fabricating porous ceramic materials. In general, pore-forming agents can be categorized into: (i) synthetic organic matters (polymer beads, organic fibres etc.), (ii) natural organic matters (starch materials, cellulose, cotton etc.), (iii) metallic and inorganic matters (nickel, carbon, fly ash, glass particles etc.), and liquid (water, gel, emulsions etc.) [19].

In their review, Eom *et al.* reported the various means of removing the pore former out of the ceramic matrix [18]. Synthetic and natural organic materials are mostly ejected through a decomposition process by applying heat treatment within a range of 200–1000°C, liquids are removed through freeze drying, salts are removed through leaching using water, carbon and silica templates are ejected through oxidation and chemical leaching respectively. It is worth noting that with different formulations and particle geometry of pore formers, the usage of the pore-forming agent method gives adequate room for the tailoring of the pore cavities in the microstructure of the developed porous ceramic materials.

Various investigators have reported the development of highly porous ceramics with starch materials (cassava, potato, wheat, rice etc.) as pore-forming agents [25–27]. In their investigation, Markovska *et al.* reported the fabrication of porous mullite ceramics by employing aluminum oxide waste as the ceramic matrix and rice husk as both the pore former and the silica source

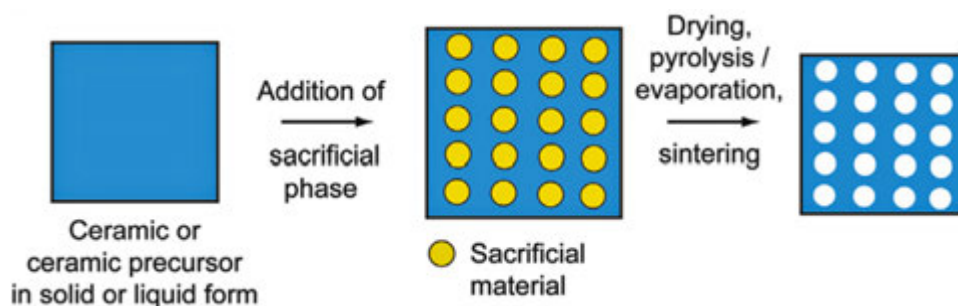


Fig. 2 Pore-forming agent method for fabricating porous ceramics. Reproduced from Hammel, E.C., Ighodaro, O.R., Okoli, O.I., 2014. Processing and properties of advanced porous ceramics: An application based review. *Ceramics International* 40 (10), 15351–15370.

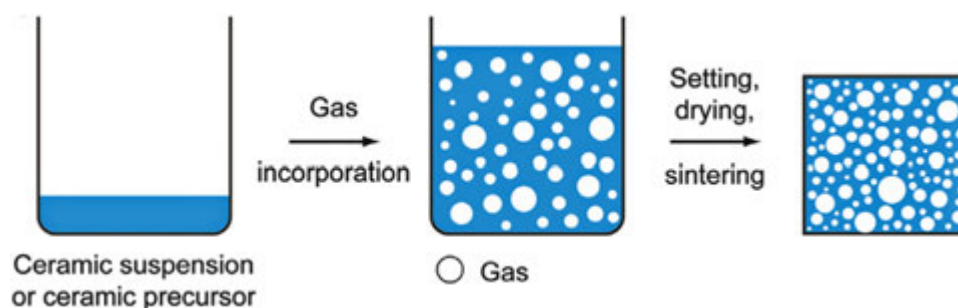


Fig. 3 Direct foaming method for fabricating porous ceramics. Reproduced from Hammel, E.C., Ighodaro, O.R., Okoli, O.I., 2014. Processing and properties of advanced porous ceramics: An application based review. *Ceramics International* 40 (10), 15351–15370.

after the burning out process [28]. Mohanta *et al.* developed porous alumina ceramics having durable strength and hierarchical pore cavities by tailoring the size and content of rice husk pore formers [29]. Elsewhere, the use of NaCl salt as pore former for the development of porous Ti_2AlC ceramics having controlled porosity was investigated by Hu *et al.* [30].

Direct Foaming Method

The direct foaming method for developing porous ceramics entails the foaming of ceramic suspension using blowing agents such as air or gas for stabilizing the foam. Thereafter, the foam is dried and then subjected to a sintering process to obtain the consolidated porous ceramics (see Fig. 3). The direct foaming technique is regarded as a low-cost and an easy means of producing porous ceramics having up to 95% porosity level [19]. Meanwhile, there are two major categories of blowing agents; physical blowing agent and chemical blowing agent [18]. The utilization of chemical blowing agent leads to a chemical reaction that produces gaseous products, while in the case of the physical blowing agent, the bubble/foam-making process is reversible and does not support any chemical reaction.

Fukushima and Colombo developed macro-cellular porous SiC foams by utilizing a mixture of polycarbosilane (PCS) pre-ceramic polymer and a chemical blowing agent (azodicarbonamide) [30]. The mixture was prepared through the ball milling process followed by foaming the mixture close to the melting temperature of the PCS. Afterwards, the foamed PCS was subjected to a curing process and then pyrolyzed at 200°C and 1000°C respectively after which the open macro-cellular ceramic materials were foamed. For the developed porous ceramics, the authors registered porosity and cell size ranges of 59–85 vol% and 416–1455 μm respectively which implies that the method can be effectively used to produce porous ceramics with tailored pore size and porosity. Through the modification of the traditional foaming technique, Barg *et al.* developed porous ceramics with interconnected pore structures (size = 0.5–3 mm and porosity $\leq 97.5\%$) by infusing foams in a ceramic suspension through the evaporation of emulsified alkaline droplet blowing agent [31,32].

Porosity and Microstructural Characterization of Porous Ceramic Materials

The possibility of controlling the porosity parameters has shown to be highly essential to maintain an appreciable strength integrity of porous ceramics. Thus far, several investigators have employed the linear intercept method of ASTM E112 [33] and mercury porosimetry [34] for characterizing the pore cavities, while the density and porosity parameters of the porous ceramics have been measured according to Archimedes' principle (ASTM C20, [35]) as represented in the equations below;

$$\rho = \frac{m_{dry} \times \rho_{water}}{m_{wet} - m_{suspended} + m_{wire}} \quad (1)$$

$$P_{open} = \frac{m_{wet} - m_{dry}}{m_{wet} - m_{suspended} + m_{wire}} \times 100 \quad (2)$$

$$P_{total} = \left(1 - \frac{\rho}{\rho_{theoretical}}\right) \times 100 \quad (3)$$

where m_{dry} is the dry mass of specimen, $m_{suspended}$ is the mass of the specimen immersed in water, m_{wet} is the mass of wet specimen, m_{wire} is the mass of the suspending rope, ρ_{water} is the density of water, P_{total} is volume fraction of total porosity of sample and P_{open} is volume fraction of open porosity of the sample.

Metallographic specimen preparation has been employed over the years by several investigators to prepare porous ceramic samples for a comprehensive microstructural evaluation. With this technique, porous ceramic samples are subjected to various process in the following order; grinding, polishing, etching and microscopic evaluation. Considering the prevalence of surface imperfections and the delicate structure of pore cavities in the sintered porous ceramics, it is imperative to employ the fine grinding (1200 and 4000 μm SiC papers) and polishing processes for the preparation of porous ceramics free from scratches, sintering defects and ultimately to prevent pore cavity blockage. Although optional, etching is performed to obtain a clear microstructure relative to the polished sample by employing either the chemical etching method (highly aggressive and hazardous reagents) or the thermal etching method (polished sample is heated up to approx. 200°C of the sintering temperature) [36].

The major microscopic technique that can be employed for the microstructural evaluation of porous ceramic materials is the electron microscope which includes both the scanning electron microscope (SEM) and the transmission electron microscope (TEM). The scanning electron microscope is often used to view and measure the microstructure and the pore geometry of porous ceramic materials respectively. Meanwhile, sputter coating of samples with ultra-thin electrically conductive metals such as gold, platinum, silver, chromium etc., is essential due to the low electrical conductivity of ceramic materials and the presence of pore cavities which promote the buildup of electrostatic charges thereby leading to electron beam deflection and charging effect. Hence, the coating serves as a conductive layer of metal on the porous ceramic sample thereby inhibiting charging effect and promoting secondary electron signal required for the microstructural analysis in the SEM.

Moreover, the granular microstructure of porous ceramic composites, in particular, those reinforced with metals can be observed using the transmission electron microscope. In order to conduct this analysis. The focused ion beam (FIB) alongside the SEM of a dual beam system are used to produce a high quality electron transparent membrane (lamella thickness < 80 nm) from the coated porous ceramic composite sample. Upon the selection of an area of interest, the ion beam is used to deposit about 0.5–1 μm thick metal line (see Fig. 4(a)). Thereafter, high beam current is used to mill large materials away from the area of interest, leaving only a tab of material to hold the specimen (see Fig. 4(b)). With the use of a micromanipulator tip, the thin lamella specimen is removed and placed on a copper grid as shown in Fig. 4(c) and (d) respectively. A magnified image of the porous ceramic specimen for TEM analysis is presented in Fig. 4(e). Fig. 5(a) and (b) respectively presents the SEM and TEM microstructures of rice husk shaped Ni-reinforced porous alumina composite.

Mechanical Properties Characterization of Porous Ceramic Materials

There are four major types of mechanical properties testing that have been employed by several researchers for characterizing porous ceramic materials. These include: flexural test, Brazilian disk test, compression test and hardness test.

Flexural Strength Test for Porous Ceramics

The flexural strength investigation is one of the most common mechanical strength tests that has been utilized over the years by researchers for measuring the bending strength capacity of porous ceramics. ASTM C1674 describes the test set-up, specimen preparation and procedures for measuring the flexural strength of advanced ceramics with engineered porosity (honeycomb cellular channels) at ambient temperature [37]. There are other ASTM standards such as ASTM C1161 and ASTM C1684 for ambient temperature testing of the flexural strength of advanced ceramics having rectangular and cylindrical geometries respectively [38,39]. The test can be carried out using both the four-point-1/4 point and three point loadings with prescribed spans and specimen geometries as stipulated in the standards above (see Fig. 6).

For rectangular shaped porous ceramic samples, the formulas for the flexural strength in four-point-1/4 point flexure and three-point flexure are;

Four-point-1/4 point flexure:

$$\sigma_f = \frac{3PL}{4bd^2} \quad (4)$$

Three-point flexure:

$$\sigma_f = \frac{3PL}{2bd^2} \quad (5)$$

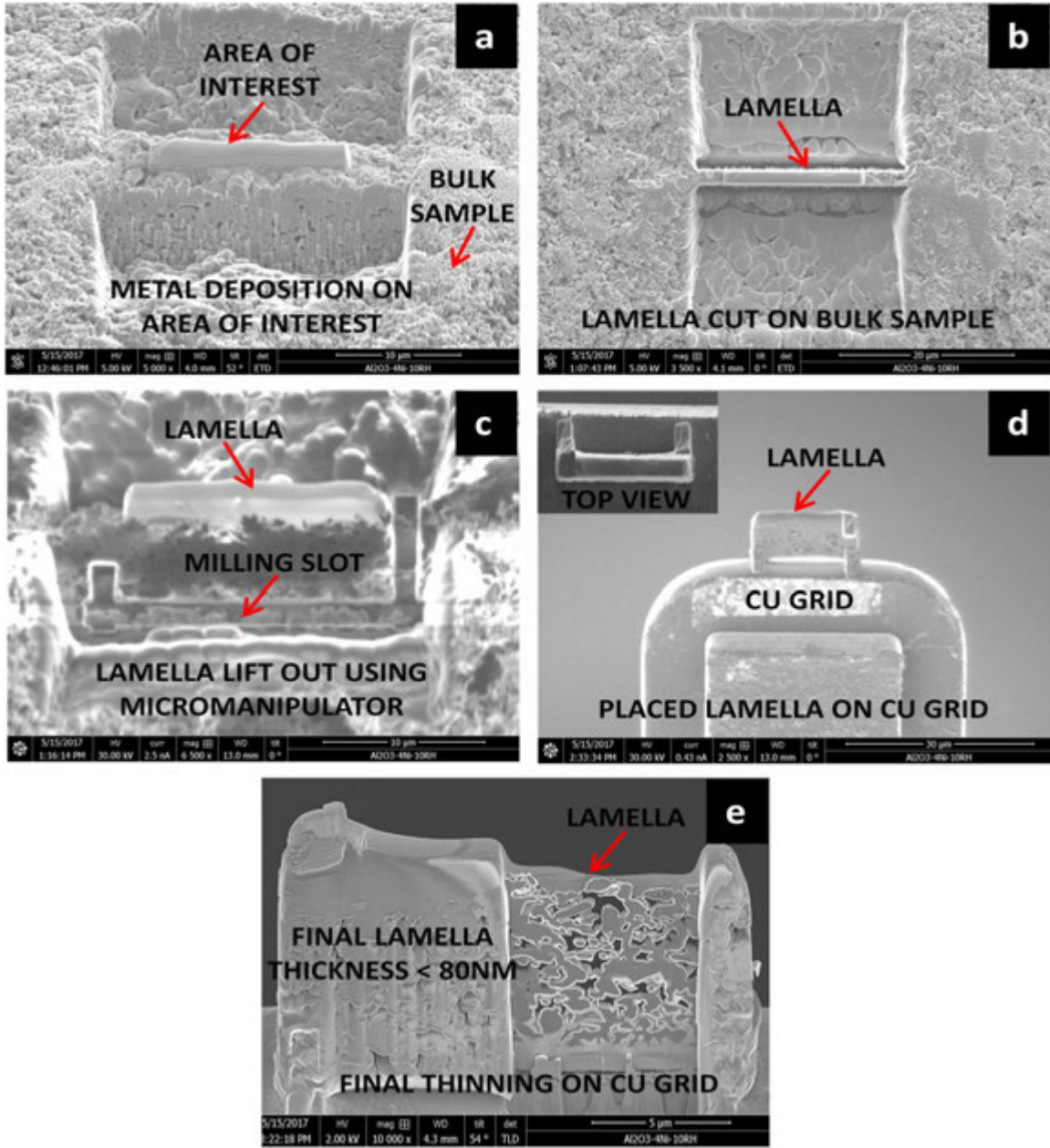


Fig. 4 Dual beam sample preparation for TEM analysis of porous ceramic materials: (a) metal deposition on area of interest, (b) lamella cut on bulk sample, (c) lamella lift out, (d) lamella placement on copper (Cu) grid, and (e) final thinning on copper grid.

For cylindrical shaped porous ceramic samples, the formulas for the flexural strength in four-point-1/4 point flexure and three-point flexure are;

Four-point-1/4 point flexure:

$$\sigma_f = \frac{4PL}{\pi D^3} \quad (6)$$

Three-point flexure:

$$\sigma_f = \frac{8PL}{\pi D^3} \quad (7)$$

where P is the break force (N), L is the outer (support) span (m), b, d and D are the width (m), thickness (m) and diameter (m) of specimen respectively.

By employing the three-point method, Ding *et al.* and Hu *et al.* measured the flexural strengths of YbF₃-reinforced porous Si₃N₄ ceramics (up to 269.87 MPa) and plain porous Si₃N₄ ceramics (50.17 MPa) respectively [40,41]. Similarly, the three-point method

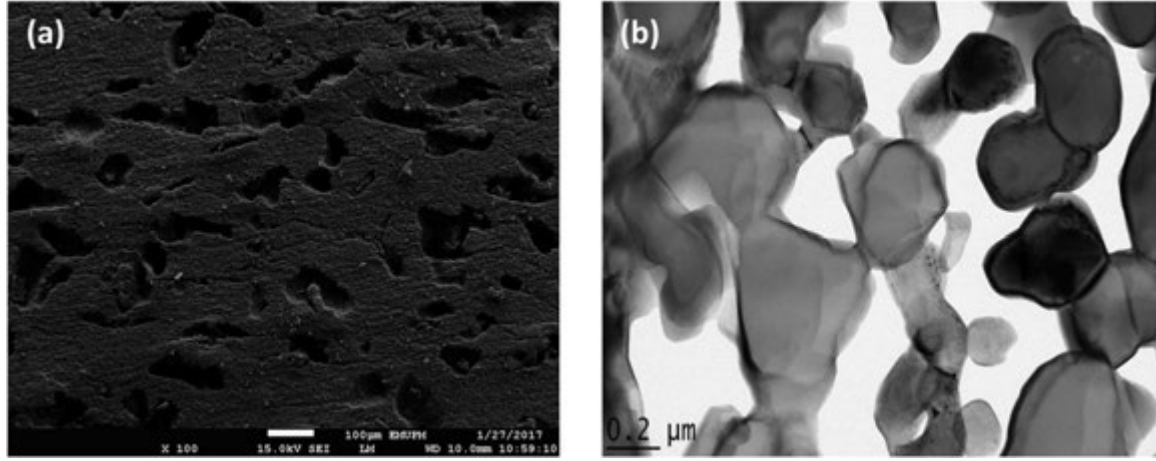


Fig. 5 (a) SEM image for pore morphology, and (b) TEM image for granular microstructure of rice husk shaped Ni-reinforced porous alumina composite.

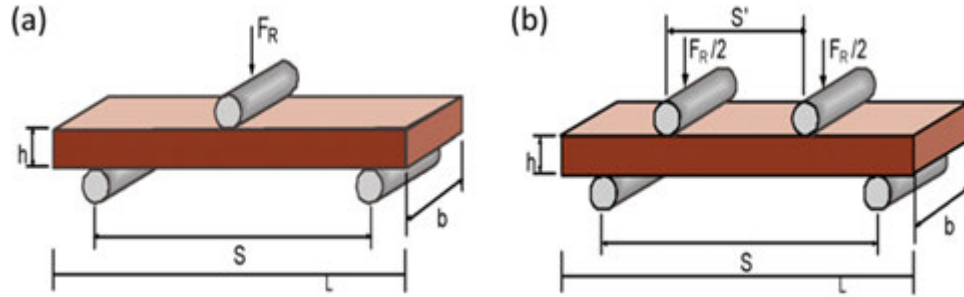


Fig. 6 Schematic diagram of the experimental (a) three-point flexure and (b) four-point flexure. Reproduced from Amorós, J.L., Cantavella, V., Jarque, J.C., Feliú, C., 2008. Green strength testing of pressed compacts: An analysis of the different methods. *Journal of the European Ceramic Society* 28 (4), 701–710.

was used by Xing *et al.* to obtain flexural strength as high as 50.17 MPa for mullite rod-enhanced porous SiC ceramics [42]. Elsewhere, the four-point method was utilized by Xiao *et al.* and Liu *et al.* to obtain the flexural strengths of bioactive glass (13–93) scaffold (34 MPa) and porous SiC ceramics (20 MPa) respectively [43,44].

4.2 Compressive Strength Test for Porous Ceramics

The compressive stress investigation is another predominant system of testing that has been adopted over the years by researchers for determining the compressive load bearing capacity of porous ceramic materials. There are existing ASTM standards such as ASTM C1424 and ASTM C365/C365M for testing monotonic compressive strength of advanced ceramics at ambient temperature and for compressive properties of sandwich cores respectively [45,46]. However, due to some limitation factors in the category of ceramics to be investigated, alternative test configuration may be followed [47]. Dam *et al.* proposed a deformation-mode map for open cell alumina wherein the compressive strength was measured by retrieving from the graph the point where the load reached the maximum value before the onset of substantial crushing of the specimen [48].

The average compressive strength and compressive strain can be computed by dividing the applied axial load by the surface area of sample and dividing the applied displacement by the sample thickness respectively.

$$\sigma_c = \frac{4P}{\pi D^2} \quad (8)$$

$$\varepsilon_c = \frac{d}{t} \quad (9)$$

Where P is the load (N), D and t are the diameter (m) and the thickness (m) of the disk respectively, and d is the actuator displacement (m).

Neeraj *et al.* employed ASTM C365/C365M to determine the compressive properties of porous ceramics with a duplex pore structure [49]. For samples that exhibited higher porosity values, the investigators utilized the deformation-mode map of open cell

ceramics to measure the compressive stress where the plateau region before the occurrence of densification was selected as the compression strength of the sample. Ma *et al.* reported a rising trend in the compressive strengths of porous whisker-structured mullite ceramics with increasing sintering temperature and subsequently observed a decline in the compressive strength values as porosity increased for each sintering temperature used [50]. From their investigation on mechanical properties of porous calcium phosphate scaffolds, Jo *et al.* reported high compressive strength value of 12.3 MPa at a high porosity of 73 vol%, whereas the compressive strength dropped to 4.8 MPa when porosity rose to 82 vol% [51].

Brazilian Disk Test for Porous Ceramics

The Brazilian disk test (also known as diametral compression test or indirect tensile test) is a common test employed for the tensile strength measurement (see Fig. 7) of brittle materials such as rocks, concrete, polymers and ceramics [52,53]. ASTM D3967 and ASTM C496/496M describe the testing apparatus, specimen preparation, and procedures for determining the splitting tensile strength of rock and concrete specimens respectively by diametral line compression of a disk-shaped specimen [54,55]. Upon employing the Brazilian disk test for the tensile strength measurement of compacted clay, Akin and Likos highlighted the advantages of this method over direct (uniaxial) tension testing methods. These include (i) ease of specimen preparation, handling and loading equipment, and (ii) high possibility of utilizing small specimen geometries which creates better consistency as well as less sensitivity to boundary conditions or heterogeneity [56].

In their investigation, Sgambitterra *et al.* highlighted the mathematical expressions (Eqs. (10)–(20)) to describe the stress states for an isotropic 2D disk under diametral compression by concentrated loads [57].

$$\sigma_x = \frac{2P}{\pi t} \left(\frac{\cos\theta_1 \sin^2\theta_1}{r_1} + \frac{\cos\theta_2 \sin^2\theta_2}{r_2} \right) - \frac{2P}{\pi D t} \quad (10)$$

$$\sigma_y = \frac{2P}{\pi t} \left(\frac{\cos^3\theta_1}{r_1} + \frac{\cos^3\theta_2}{r_2} \right) - \frac{2P}{\pi D t} \quad (11)$$

$$\tau_{xy} = \frac{2P}{\pi t} \left(\frac{\cos^2\theta_1 \sin\theta_1}{r_1} + \frac{\cos^2\theta_2 \sin\theta_2}{r_2} \right) \quad (12)$$

$$r_2^2 = r_1^2 + D^2 - 2r_1 D \cos\theta_1 \quad (13)$$

$$\cos\theta_2 = \frac{D^2 + r_2^2 - r_1^2}{2r_2 D} = \frac{D - r_1 \cos\theta_1}{r_2} \quad (14)$$

$$\sin\theta_2 \sqrt{1 - \cos^2\theta_2} = \frac{r_1 \sin\theta_1}{r_2} \quad (15)$$

$$x = r_1 \sin\theta_1 \quad (16)$$

$$y = \frac{D}{2} - r_1 \cos\theta_1 \quad (17)$$

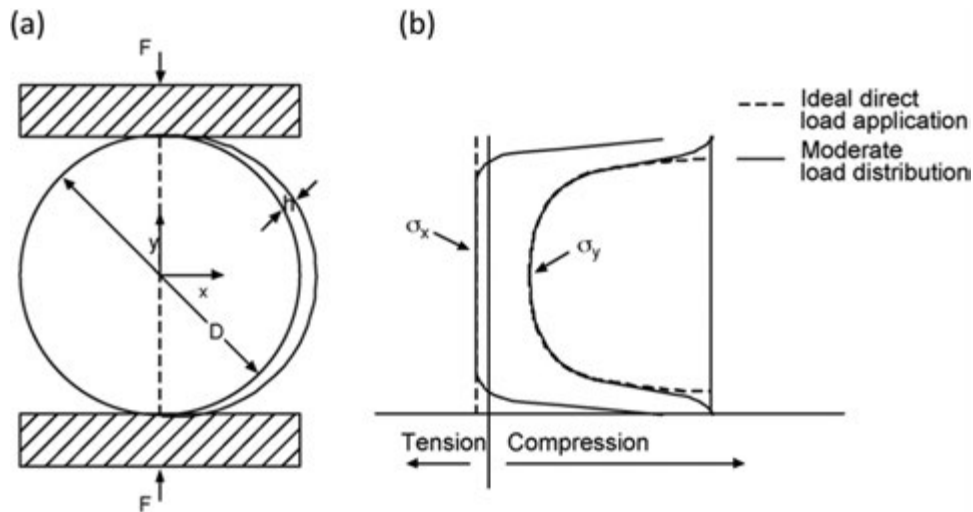


Fig. 7 Brazilian disk test (a) experimental device with direct load application and (b) stress distribution along the vertical diametral plane. Reproduced from Amorós, J.L., Cantavella, V., Jarque, J.C., Feliu, C., 2008. Green strength testing of pressed compacts: An analysis of the different methods. *Journal of the European Ceramic Society* 28 (4), 701–710.

By substituting Eqs. (13)–(17) in Eqs. (10)–(12), the Equations become:

$$\sigma_x = \frac{2P}{\pi t} \left[\frac{\left(\frac{D}{2} - \gamma\right)x^2}{\left(\left(\frac{D}{2} - \gamma\right)^2 + x^2\right)^2} + \frac{\left(\frac{D}{2} + \gamma\right)x^2}{\left(\left(\frac{D}{2} + \gamma\right)^2 + x^2\right)^2} - \frac{1}{D} \right] \quad (18)$$

$$\sigma_y = \frac{2P}{\pi t} \left[\frac{\left(\frac{D}{2} - \gamma\right)^3}{\left(\left(\frac{D}{2} - \gamma\right)^2 + x^2\right)^2} + \frac{\left(\frac{D}{2} + \gamma\right)^3}{\left(\left(\frac{D}{2} + \gamma\right)^2 + x^2\right)^2} - \frac{1}{D} \right] \quad (19)$$

$$\tau_{xy} = \frac{2P}{\pi t} \left[\frac{\left(\frac{D}{2} - \gamma\right)^2 x}{\left(\left(\frac{D}{2} - \gamma\right)^2 + x^2\right)^2} + \frac{\left(\frac{D}{2} + \gamma\right)^2 x}{\left(\left(\frac{D}{2} + \gamma\right)^2 + x^2\right)^2} - \frac{1}{D} \right] \quad (20)$$

Meanwhile, based on the ASTM standards (ASTM D3967 and ASTM C496/C496M), the tensile stress is obtained at the center of the disk $x=0, \gamma=0$, and it is tensile along the x direction i.e., substituting these values to Eq. (18), σ_x stress reaches its maximum tensile value and can be expressed as follows:

$$\sigma_t = \frac{2P}{\pi Dt} \quad (21)$$

Where P is the load (N), D and t are the diameter (m) and the thickness (m) of the disk respectively.

Similarly, the tensile strain can be evaluated from Eq. (22).

$$\varepsilon_t = \frac{d}{D} \quad (22)$$

Where d is the actuator displacement (m).

More so, the Young's modulus which represents the slope of the initial straight line portion of the tensile stress- tensile strain plot (Hibbeler and Fan) can be expressed as [58]:

$$E = \frac{\sigma}{\varepsilon} \quad (23)$$

Meanwhile, with the aim of obtaining a high consistency level in the results as well as agreement with theories of brittle failure with respect to specimen size effects, Kumar and Prashanth and Sandoval *et al.* proposed that the ratio between the thickness and diameter $\frac{t}{D}$ of the ceramic disk must be kept within a range of 0.2–0.25 in order to ensure that fracture is initiated by tensile stress only [59,60]. Also worth noting is the fact that the $\frac{t}{D}$ ratio highlighted above falls within the range (0.2–0.75) suggested in the ASTM D3967 and ASTM C496/C496M standards. More so, it is essential to ensure even distribution of the applied load as well as reduced friction between the specimen and platen to a bearable level. In this regard, use of padding materials and lubricant paste have been suggested by Sandoval *et al.* and Fahad [61,62].

Tallon *et al.* showed that the tensile strength of highly porous alumina ceramics declined with increasing pore size where samples with “small pore” and “big pore” morphologies exhibited 5 MPa and 12 MPa respectively [63]. Hernandez *et al.* and Sandoval *et al.* utilized the Brazilian test to evaluate the tensile strength and the Young's modulus of porous ceramic materials which was measured from the slope of the linear part of the stress-strain curve [60,64]. Generally, the investigators above observed a decline in the tensile strength and Young's modulus values with rising porosity.

Substantiating further into the details of the test, the typical fracture patterns exhibited by the broken disks are as follows [60,65]:

- Triple-cleft Fracture (TCF): The pattern is characterized by a central fissure running along the diametral axis of the load (diametral fracture, DF) together with secondary cracks that propagate parallel to the central fissure and break it in three or more fragments due to the additional failure of the internal fragments.
- Load Region Fracture (LRF): This pattern occurs between the disk and compression platens. It consists of the presence of shear prism at generator culminating with small flakes from the disk detached from the cylinder surface adjacent to the contacting platen. Meanwhile, a complete fragment of the disk can become separated in severe cases.
- Combination of DF and LRF.

Hardness Test for Porous Ceramics

The hardness measurement is another important testing procedure that has been adopted over the years by researchers for determining the resistance level of porous ceramic materials to frictional forces such as abrasion. The ASTM standard, ASTM C1327 has been regularly used as the standard test method for Vickers indentation hardness of advanced ceramics [66]. The value of the hardness (HV number) can be determined by the following equation:

$$HV = \frac{1.8544F}{d^2} \quad (24)$$

Where F is the applied load (N) and d is the average length (m) of the two diagonals left by the indenter.

By utilizing different pore-forming agents for preparing porous alumina ceramics, Ali *et al.* reported a decrease in the hardness values from 172.6 to 38.1 HV and 160.6–15 HV with increasing porosity for samples shaped with graphite (37.3%–61.1%) and yeast (30.2%–63.8%) pore-forming agents respectively [67]. Whereas, the hardness values varied for samples shaped with rice husk ash due to reaction between alumina and rice husk ash to form mullite. Similarly, Nam *et al.* observed a decline (932–7 HV) with rising porosity (53%–73%) [68]. Li *et al.* reported that despite the rising content (4–20 wt%) of the CaSO_4 -dextrin body-forming agent, the Vickers hardness values of porous alumina samples exhibited gradual decline from 0.53 to 0.56 GPa to 0.49–0.53 GPa owing to the slight porosity increase from 48%–49% to 51%–53% [69]. Employing a numerical study, Chen and Brandon reported the consistency of porosity-dependence of the hardness with values predicted using empirical expressions [70].

Conclusions

In this work, a documentation of the fabrication methods and characterization techniques for porous ceramic materials is presented. The article comprehensively reveals both reliable and low-cost fabrication techniques for developing porous ceramics. Fabrication techniques such as the pore-forming agent method has been highlighted as an economically viable method for lab-scale development of porous ceramic materials. More so, requisite standards alongside supporting investigations on the characterization of porosity, microstructure and mechanical properties have been presented in this article. Overall, the article presents the necessary information required for the development of highly robust porous ceramic materials for use in present-day applications such as thermal insulation systems, separation membranes, catalyst supports and others.

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Factors Affecting the Porosity and Mechanical Properties of Porous Ceramic Composite Materials

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Introduction

There are many industrial applications of porous ceramic material as filtering material, including use as a membrane for separation, light weight structural materials [1], catalyst supports, thermal insulation, bioreactors, gas filters for high temperature [2,3], medical ultrasonic imaging, and underwater sonar detectors [4,5]. The unique properties of porous ceramics with a tailored microstructure, such as good strain and damage tolerance, good thermal shock resistance, wear resistance, high corrosion and light weight, result in porous ceramics having potential application as structural materials [6,7]. In general, it is known that with the increasing porosity of porous ceramics the mechanical properties decrease. However, at the same time, most applications of porous ceramics need to have good mechanical properties [8]. Therefore, in the case of the filtration of hot gas and molten metal, the fluctuation of temperature during the process will leave the materials liable to thermal shock. During service, the mechanical properties of the filter must be high enough to bear the operation pressure, and also the filter properties must not deteriorate with the increase in temperature. In addition, the range of temperature (260–900°C) in the filtration process is considered in the filtration of hot gas and these filters may face pressures of up to 8 MPa. Because filtration occurs under these conditions, it is important that the filters of ceramics have sufficient mechanical strength and thermal shock resistance [9]. In addition, researchers have mainly focused on the mechanical properties of porous materials [10]. Many authors have reviewed porous ceramic materials under different topics. Studart *et al.* [11] reviewed the processing routes of macro-porous ceramics, Chevalier *et al.* [12] provided a review of the fabrication of porous substrates, while Ohji and Fukushima [13] also reviewed macro-porous ceramics. Although there have been much research works on porous composite ceramic materials, there are no research studies performing a comparison of these works for the identification of drawbacks and weak links as areas for improvement. This lack of information is a serious drawback for further development in the area of porous ceramic composite materials. Therefore, this research has been conducted to fill that gap with the necessary knowledge. The main aim of the present paper was to review in detail the factors affecting the porosity of ceramic material, such as pore forming agents, the mechanical properties of porous ceramic material, such as the sintering temperature, ceramic additives, and metal particle additives, the degree of oxidation, solid content, and coating. On the other hand, some factors were used to improve the machinability to render the porous ceramic composite materials easy to machine. Fig. 1 illustrates the R&D aspects of porous ceramics that include important factors affecting the porosity and the mechanical properties of porous ceramic composite materials.

Features of Porous Ceramic and Standard Characteristics

This section is intended to highlight the significant features of porous ceramics, such as the pore size and porosity ratio, and the applications and methods of producing porous ceramic composite materials. In general, porous ceramics can be classified into three grades according to the pore diameter: (1) micropore ceramics in the range of $d < 2$ nm, (2) meso-pore ceramics in the range of $50 \text{ nm} > d > 2$ nm, and (3) macro-pore ceramics in the range of $d > 50$ nm [11,13]. For example, meso- and macro-pore ceramics are desired in sensors and catalysis to supply a high surface area and to improve the accessibility of liquids and gases to reactive areas. Small pores in the range of 50–100 nm are desired to provide physical cues that promote differentiation, proliferation, the migration of cells, and finally quick healing. Large pores > 300 – $400 \mu\text{m}$ with hierarchical structures are desired in regenerative medicine for implanted scaffold vascularization [14]. In addition, there are many methods for fabricating porous ceramic, such as partial sintering, sacrificial fugitives, replica templates, direct foaming, etc. [13]. Table 1 presents some of the methods that have been used in the literature to produce one type of porous ceramics, i.e., those known as macro-porous ceramics. Fig. 2 shows the classification of porous ceramics according to pore size, applications and fabrication methods.

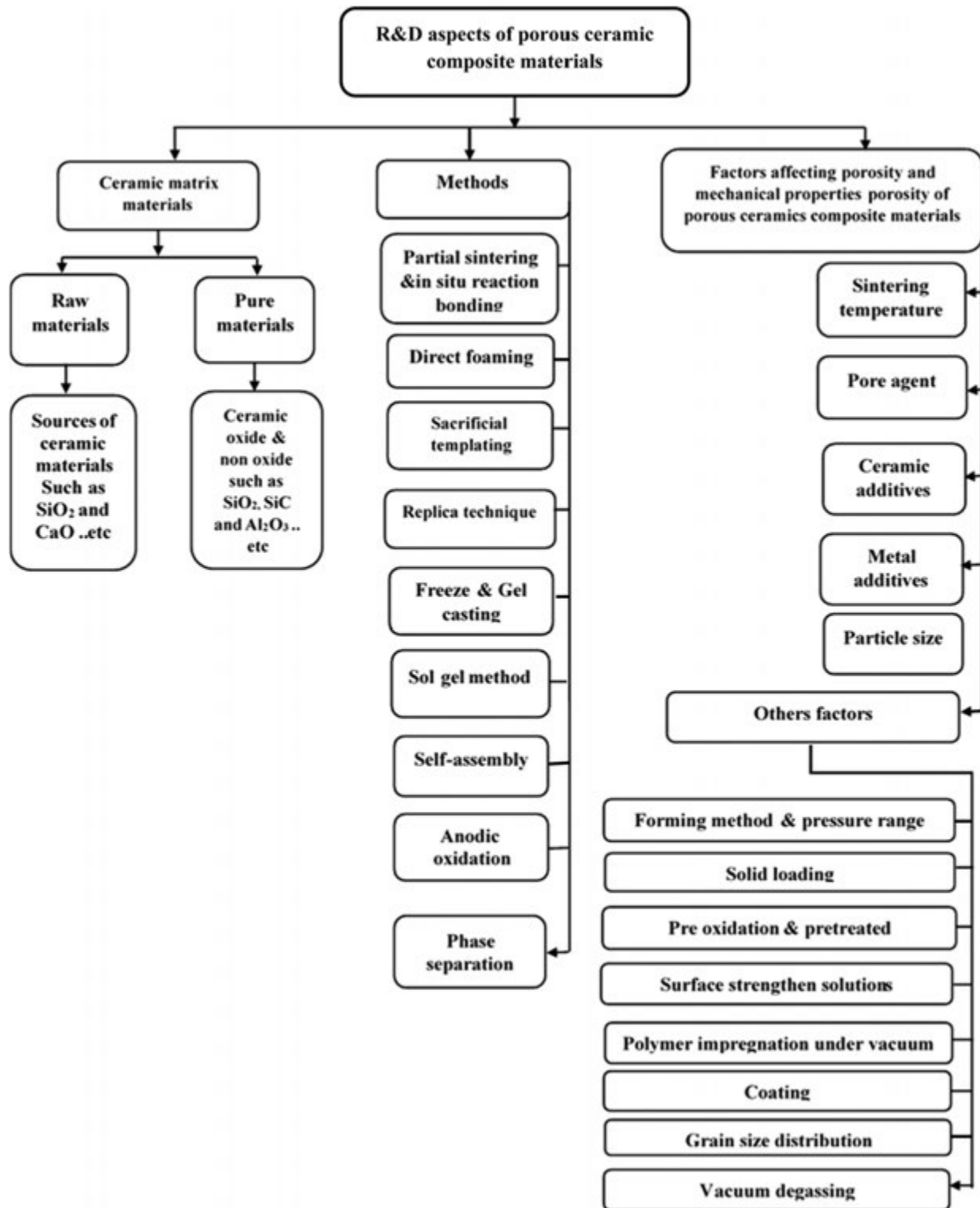
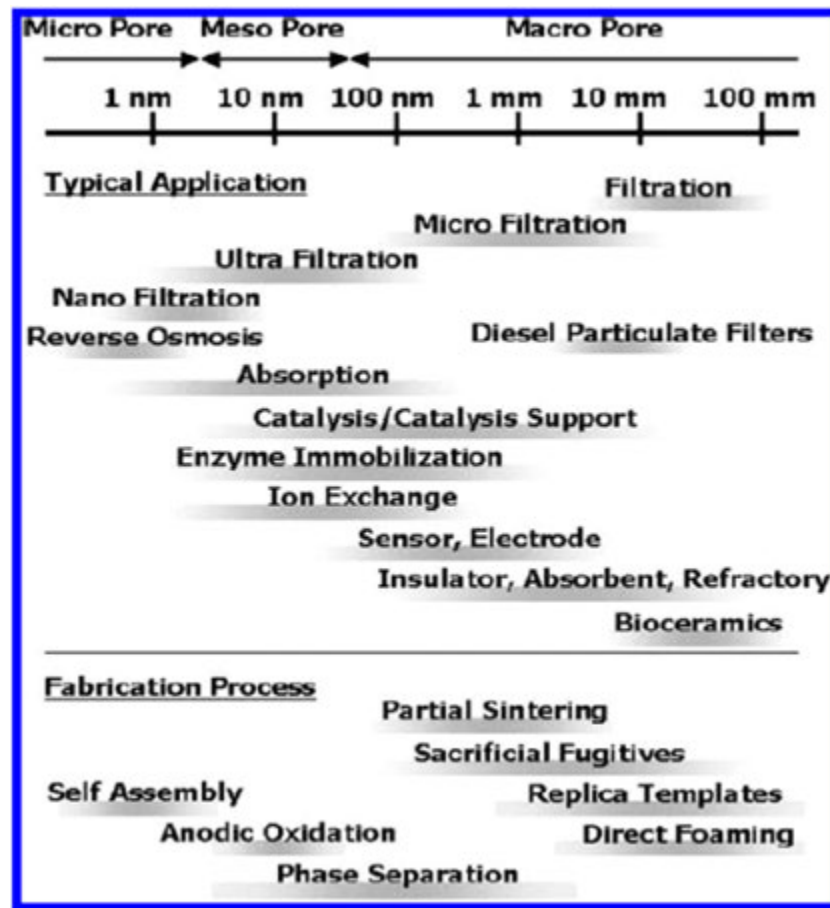


Fig. 1 R&D aspects of porous ceramic composite materials including the important factors affecting porosity and the mechanical properties of porous ceramics composite materials.

Table 1 Some methods that have been used to produce macro-porous ceramics [7,15]

Method	Porosity range	Pore size average	Advantages	Limitations
Sacrificial fugitives	20–90%	From 1 to 700 μm	Well-turned size and shape of pore	Low interconnectivity among the pores
Partial sintering	Usually below 50%	2 to 5 times smaller than raw powder < 10 μm	Narrow size distribution and simple method	Pore size is limited by sinterability of coarse powder, porosity range is limited to 50%
Replica template	40–95% by using polymer replica	From 10 to 3000 μm by using polymer replica	Interconnected large pores and high open pores	Limited mechanical performance and high pore size
Direct foaming	45–95%	From 10 to 1200 μm	Interconnected porosity and highly porous	High pore size

**Fig. 2** Classification of porous ceramics according to pore size, applications, and fabrication methods [13].

Effects of Sintering Temperature

The sintering temperature of porous ceramic materials is considered to be one of the important factors affecting their mechanical properties, microstructure, and porosity. Several studies have been performed to investigate the effect of sintering temperature on the properties of porous ceramic.

Hiroki Fujita *et al.* studied the effect of using a thermal aging process on the mechanical properties of continuous-fiber-reinforced porous ceramic composites (CFCCs) used in the industry of power generation. The results revealed that the hardness and modulus of porous mullite/alumina ceramic composites increase when using a long duration heat treatment at 1000–1200°C for 1000 h. Also, similar improvements in the tensile strength and modulus have been accrued for the composite in the ± 45 degree orientation but with no change in the strain of failure as shown in Fig. 3. By contrast, in the 0/90 degrees orientation, the modulus of the porous composite slightly increased without changes in the failure strain and the tensile strength [16].

Chi *et al.* [17] investigated how glycerol and Al_2O_3 materials affect the sintering behavior of porous silicon carbide (SiC) ceramics using yeast as a pore forming agent. It is found that glycerol can enhance the stability and the dispersion of the slurry and the sintering behavior, Al_2O_3 also has a great effect on sintering behavior of porous SiC ceramics. Thus, the flexural strength

increased from 7.6 ± 1.4 to 16.8 ± 1.2 , while the density increased from 0.93 to 1.10 g/cm³ and the porosity decreased from 68.5 to 61.4%, when the temperatures of sintering were increased from 1100 to 1300°C. Eom *et al.* [18] mentioned that the effect of sintering temperature on the mechanical properties of porous SiC was great. The results revealed that when increasing the temperature of sintering from 1800 to 1950°C at porosity 40%, both the flexural and compressive strength were increased; the flexural strength changed from 50 MPa at 1800°C to 290 MPa at 1950°C and the compressive strength changed from 50 MPa at 1800°C to 100 MPa at 1900°C. The excellent strength of these porous ceramics is owing to two reasons: the first is the decrease of the porosity from 55% at 1800°C to 40% at 1950°C, the second is the presence of a dense strut with a well-developed grain structure that transformed from equiaxed to platelet grains with a lack of macroscopic defects, as in Fig. 4.

Liu *et al.* [19] studied the effect of preheat-treated aluminosilicate (PHAS) powder on the mechanical properties of porous SiC ceramics. The study showed that with a 5.0% PHAS addition to porous SiC ceramics, the flexural strength of 86.9 MPa of these ceramics is higher than the flexural strength of 22.0 MPa of porous SiC ceramics without a PHAS addition, and the open porosity values were 35.3, 44.8%, respectively. These improvements in the mechanical properties were attributed to the enhancement of the

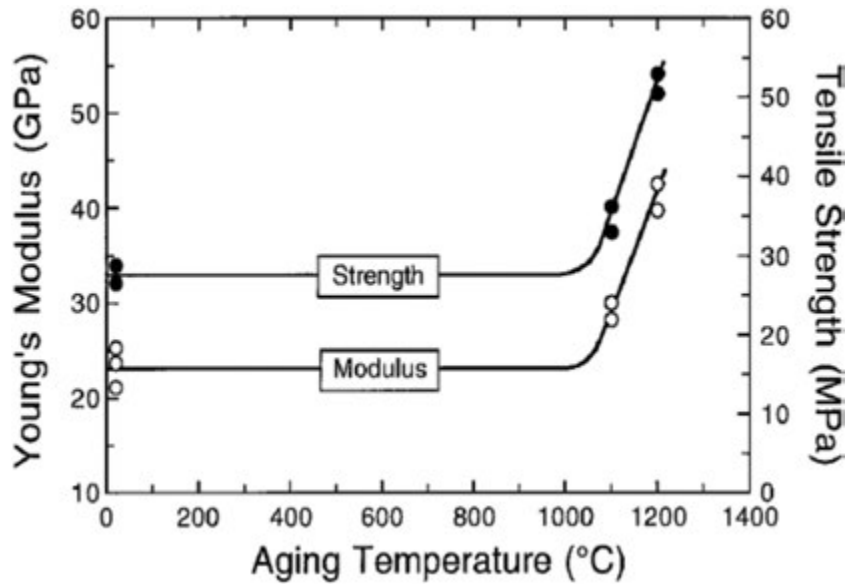


Fig. 3 Effects of aging temperature on the tensile strength and Young's modulus of porous mullite/alumina ceramic composites [16].

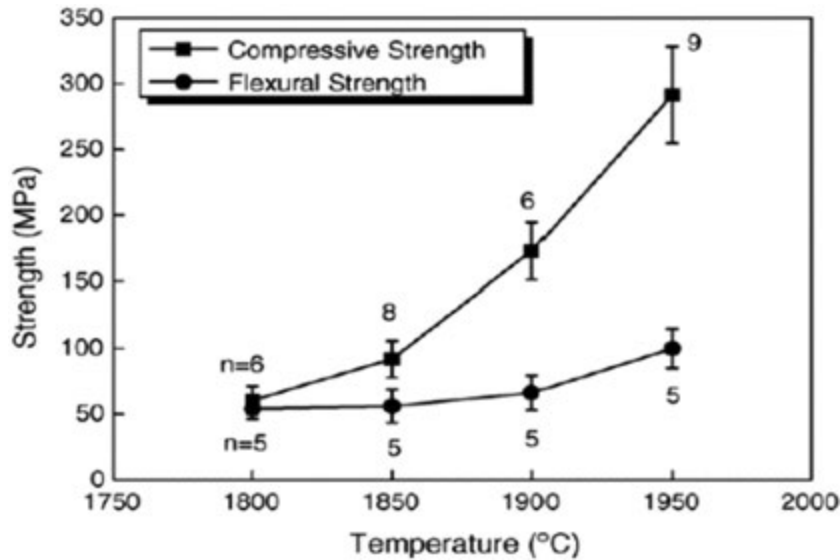


Fig. 4 Effect of sintering temperature on the flexural and compressive strengths of porous silicon carbide (SiC) ceramics. The number n in the graph denotes the total number of samples measured at each condition [18].

growth of the neck by means of PHAS and the decrease in the open porosity with the PHAS addition, because the process of mullitization was almost complete at 1450°C with the addition of 5.0 wt% of PHAS as shown in Fig. 5.

Hu and Wang [20] presented the effect of sintering temperature on the compressive strength of porous yttria-stabilized zirconia (YSZ) using the gel casting method. The results revealed that by increasing the sintering temperature from 1350 to 1550°C, the average pore size decreases and the porosity decreases from 77 to 65%, while the linear shrinkage and compressive strength increase from 15.4 to 31.8% and from 3 to 27 MPa, respectively as in Fig. 6.

This increase in the compressive strength was attributed to the decrease in porosity and pore size. Jin and Kim [21] described the use of low temperature processing for highly porous SiC ceramics to improve their flexural strength. In general, the strength decreases with increasing porosity and increases with increasing temperature of pyrolysis. For example, the flexural strength of porous SiC ceramics at 1400°C was ~32 MPa with ~71% porosity, while that for the pyrolyzed temperature at 1100°C was ~10 MPa with ~70% porosity. The study showed that with increasing temperature of pyrolysis, the flexural strength increased at the same porosity. This improvement in the flexural strength was related to the enhanced densification of the strut after pyrolysis at the higher temperature, and was also attributed to the small size of the cell (5–8 μm) and the homogeneity of the microstructure, i.e., the lack of macroscopic defects as in Fig. 7.

Yan *et al.* [22] studied the effect of sintering temperature on the pore characterization and the strength of porous alumina–mullite. The results showed that the temperature of sintering affects strongly the formation of secondary mullite which changes the characteristics of the pore and the strength. At 1500°C, secondary mullite formation has taken place with a high apparent

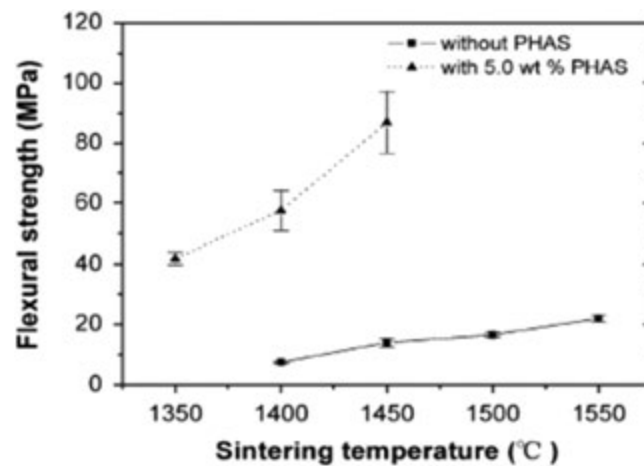


Fig. 5 Flexural strength vs. sintering temperature for porous silicon carbide (SiC) ceramics without and with 5.0 wt% preheat-treated aluminosilicate (PHAS) addition, sintered at the indicated temperature for 2 h in air [19].

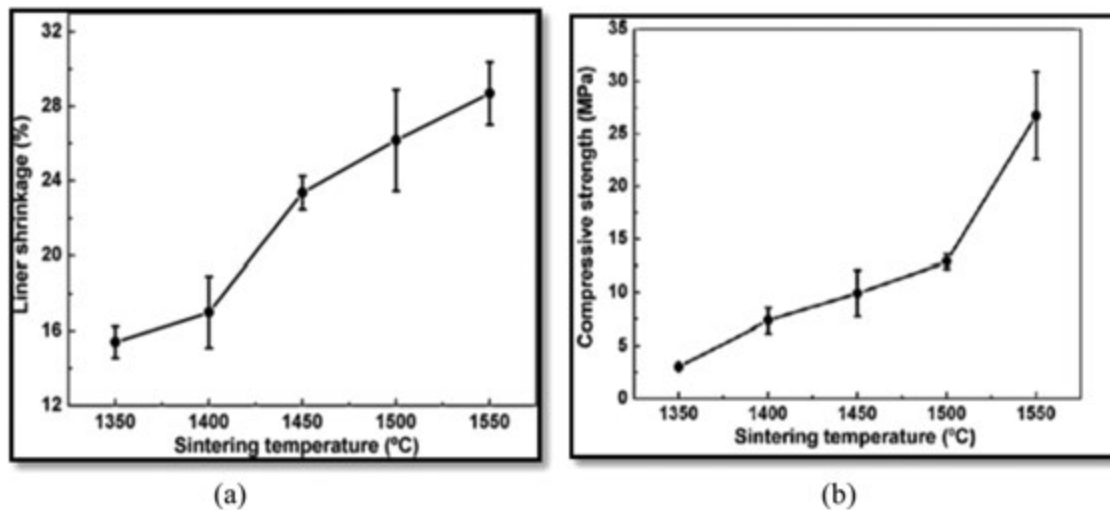


Fig. 6 (a) Variation of the linear shrinkage and (b) the compressive strength of porous Yttria-stabilized zirconia (YSZ) ceramics with sintering temperature [20].

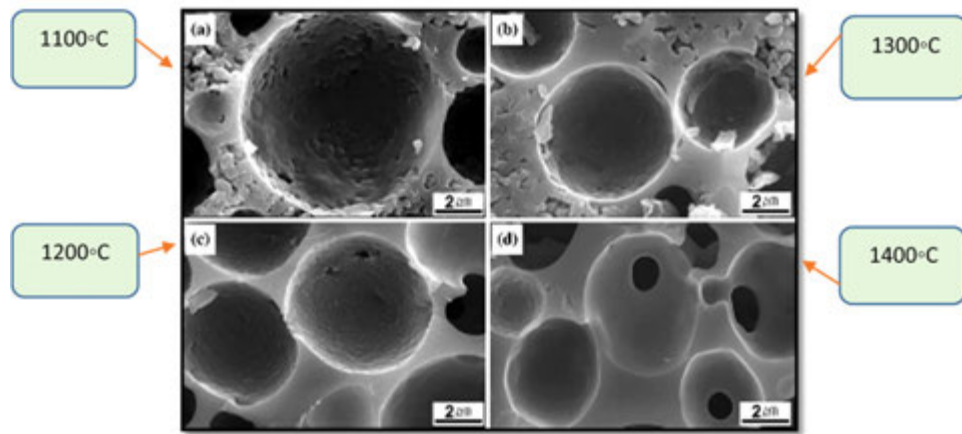


Fig. 7 Strut microstructure of the porous silicon carbide (SiC) ceramics pyrolyzed at various temperatures for 1 h in argon [21].

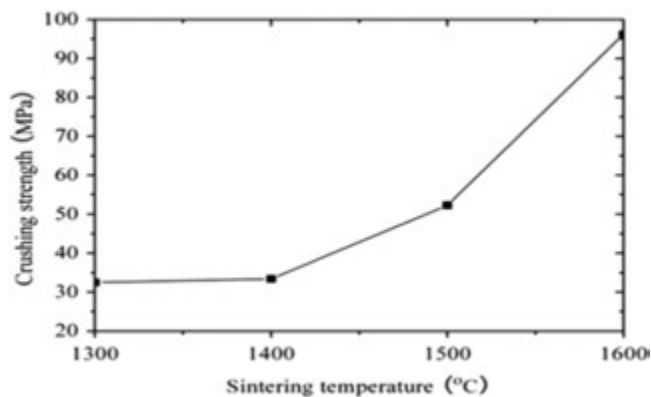


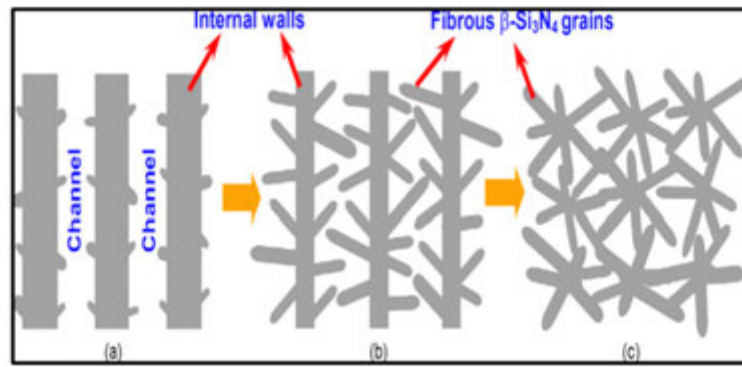
Fig. 8 Variation of crushing strength with sintering temperature [22].

porosity of 42%, a high crushing strength of 52 MPa, an homogenous distribution of pore size and a high mullite content of 86.6 wt% as shown in Fig. 8.

The improvement in the mechanical properties of porous ceramics is attributed to the formation of mullite because it has a high strength and good creep resistance [22,23]. Feng Ye *et al.* [24] explained the influence of the sintering temperature on the porosity and mechanical properties of highly porous silicon nitride (Si_3N_4) produced by the freezing casting method. The study showed no direct influence of the sintering temperature on the porosity with a change from 73.2% at 1700°C to 72.1% at 1900°C. However, the fracture toughness and the flexural strength of porous Si_3N_4 improved from 0.5 ± 1 at 1700°C to 1.1 ± 0.2 at 1900°C and from 21 ± 6 at 1700°C to 73 ± 9 at 1900°C, respectively. This is due to the changes in the pore structure and the development of the microstructure of the porous Si_3N_4 ceramics sintered at various temperatures (see Fig. 9). This unique microstructure was useful for improving the mechanical properties and also reduced the shrinkage of the porous Si_3N_4 ceramics.

Kumar *et al.* [25] studied the effect of sintering temperature and SiC and polycarbosilane (PCS) additives on the porosity and strength of polysiloxane-derived porous SiC ceramics. The study indicated that by increasing the temperature of sintering from 1800 to 1950°C, the microstructure of the porous SiC ceramics prepared using the PCS fillers shows the presence of large defects as in Fig. 8 (c). This is caused by changes in the morphology of the grains from a mixture of large faceted grains and small, equiaxed to large faceted grains and pore coalescence. The irregular morphology is also retained in the microstructure of the porous SiC using the PCS filler, while the microstructure of the porous SiC using the SiC filler shows an increase in irregular cells as in Fig. 10(a) and (b).

Generally, with an increase in the temperature of sintering, the porosity decreases and the strength increases. In addition, based on the temperature of sintering, the flexural strength of the porous ceramics prepared with PCS (16 MPa) at 59% porosity is lower than that prepared with SiC (41 MPa) at 51% porosity because of the formation of large defects in the microstructure of the porous ceramic due to the PCS filler. The excellent strength of the porous ceramic with the SiC fillers is caused by the presence of a rigid strut with good grain structure development and a lack of defects at the macroscopic level [25]. Li *et al.* [26] studied the effect of the sintering temperature on the flexural strength of porous SiC ceramics for high temperature gas filtration. The study showed that



Improvement of mechanical properties

Fig. 9 Development of microstructure for porous silicon nitride (Si₃N₄) ceramics at various temperatures [24]. (a) Sintered at 1700°C, showing only a small amount of elongated β-Si₃N₄ grains with low aspect ratio grown from the thick wall of the channels. (b) Sintered at 1800°C, showing a great number of fibrous β-Si₃N₄ grains grown from the thin internal walls of the aligned pores. (c) Sintered at 1900°C. The elongated β-Si₃N₄ grains could grow from one side of the channel to the other side and the aligned channel walls almost disappeared due to the growth of β-Si₃N₄ grains.

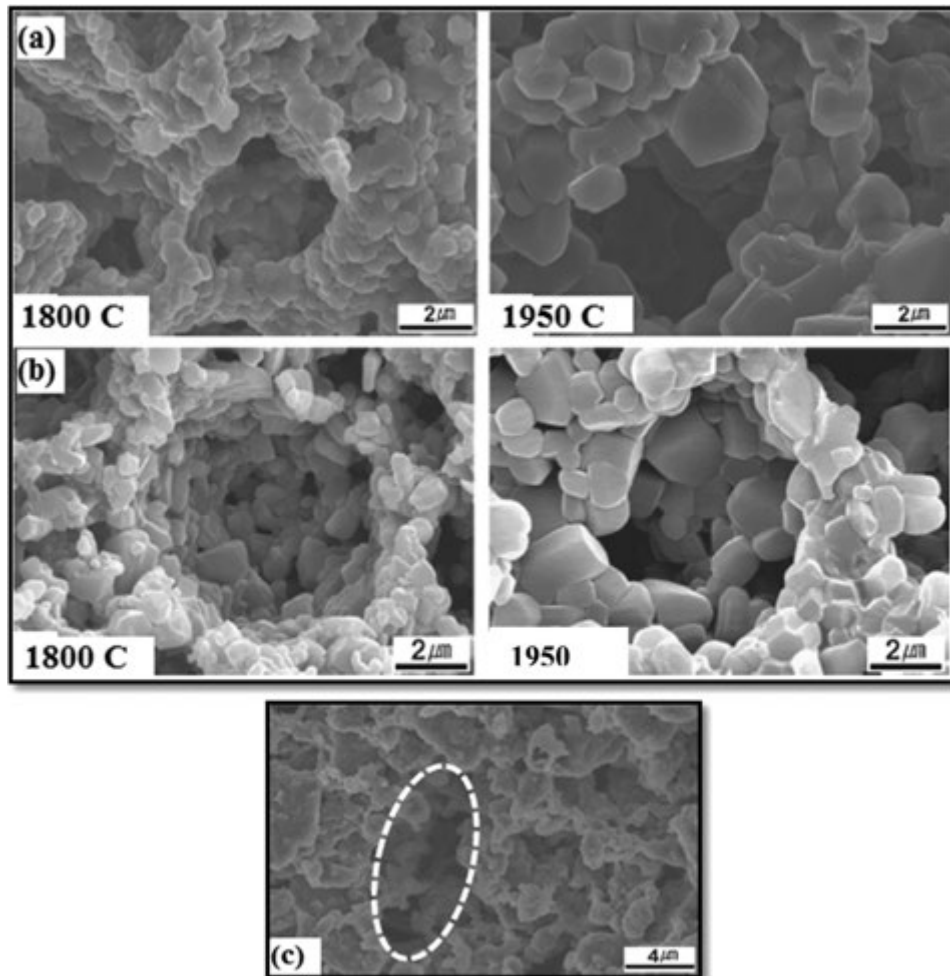


Fig. 10 Effect of sintering temperature on the grain morphology of the prepared porous silicon carbide (SiC) ceramics: (a) using the SiC filler at 1800 and 1950°C, (b) using the polycarbosilane (PCS) filler at 1800 and 1950°C, and (c) pore coalescence [25].

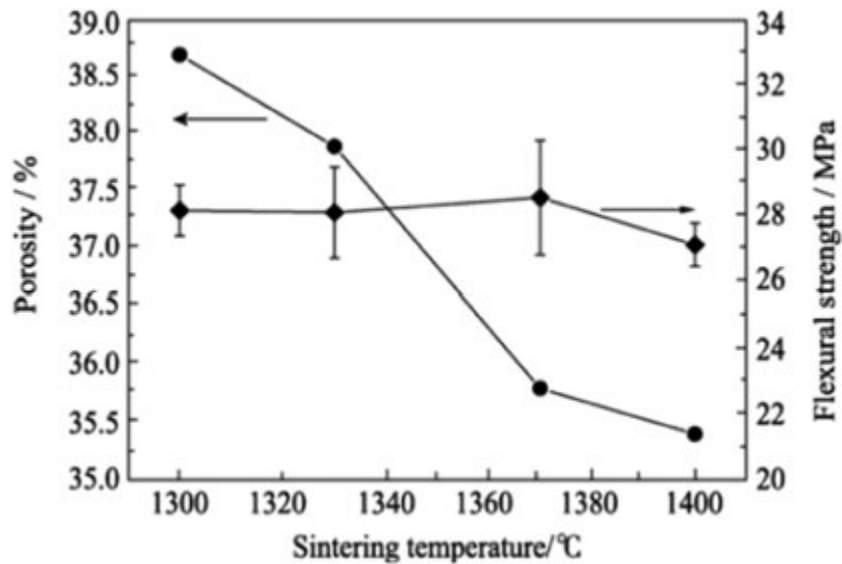


Fig. 11 Effects of sintering temperatures on the porosity and flexural strength of silicon carbide (SiC) porous ceramics [26].

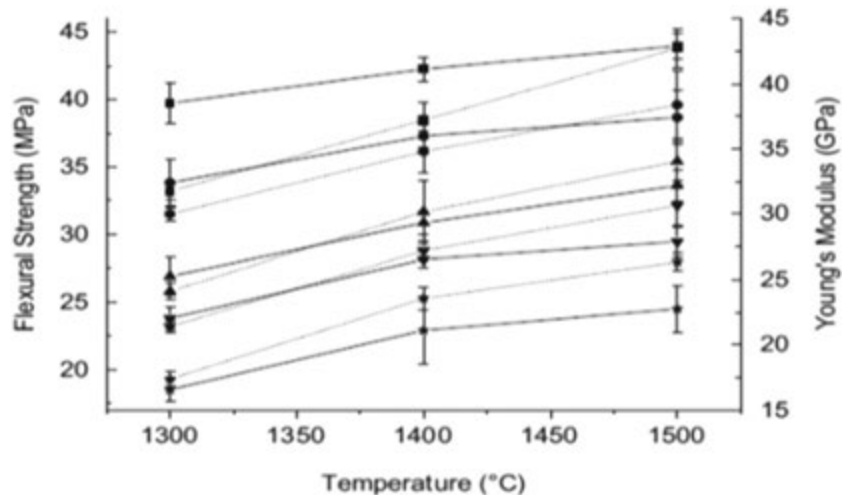


Fig. 12 Temperature dependence of flexural strength (γ) and Young's modulus of porous SiC ceramics [27].

with the sintering temperature increasing from 1300 to 1400°C, the porosity of the porous SiC ceramics decreased from 38.7 to 35.4% and the flexural strength of the porous SiC ceramics increased slightly to about 27 MPa as shown in Fig. 11.

Kayl *et al.* [27] used the liquid precursor of mullite to improve the mechanical properties of porous SiC ceramics by applying different sintering temperatures. The study showed that by increasing the sintering temperature up to 1400°C, the Young's modulus and the flexural strength increased, the range of porosity was between 31 and 48%, and the Young's modulus and the flexural strength were in the ranges of 16.6–42.9 GPa and 19.3–43.8 MPa, respectively, as in Fig. 12.

The authors reported that the reason for the improved mechanical properties of porous SiC ceramics was the formation of mullite, the SiC phases and the cristobalite phase existing in the porous ceramics. Needle-like mullite found in the porous SiC ceramics has a significant effect on the bonding of SiC particles, thus leading to an improvement in the Young's modulus and the flexural strength [27,28]. Chena and Miyamotoa [29] studied the effect of the sintering temperature on the fabrication of unique porous SiC ceramics using a sintering-decarburization process. The study showed that the porous SiC ceramics made at 600°C have a compressive strength of 101 MPa and a bending strength of 23 MPa. The porous SiC ceramics made at 1000°C have a compressive strength of 106 MPa and a bending strength of 26 MPa at a porosity of around 70%. The higher mechanical properties of porous SiC ceramics are attributed to the presence of a rigid honeycomb structure and the lack of macroscopic defects in sintered porous SiC ceramics, as in Fig. 13 [29].

Dongchen Wu *et al.* [30] mentioned the enhancement of the mechanical properties and the corrosion resistance of porous mullite ceramics using a low temperature fabrication route. The results revealed that at a sintering temperature of 1450°C for 30 wt

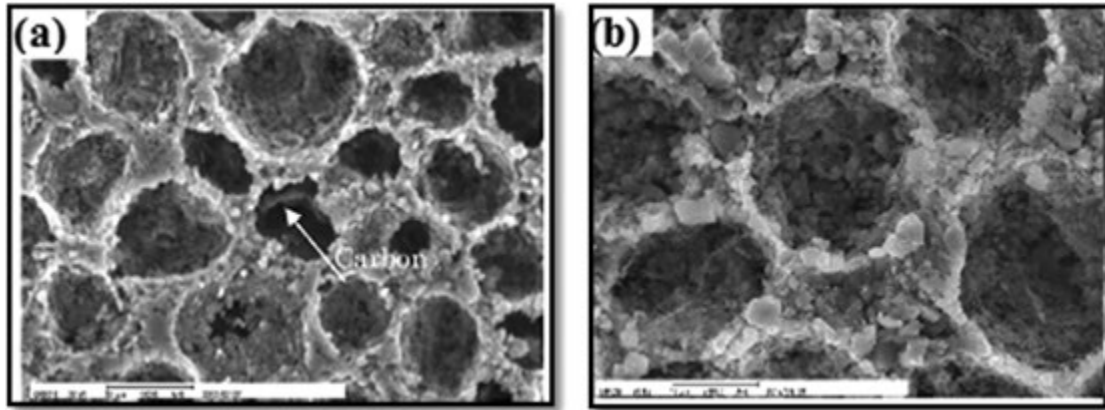


Fig. 13 Structure of rigid honeycomb (a) decarburized at 600°C for 10 h and (b) decarburized at 1000°C for 5 h [29].

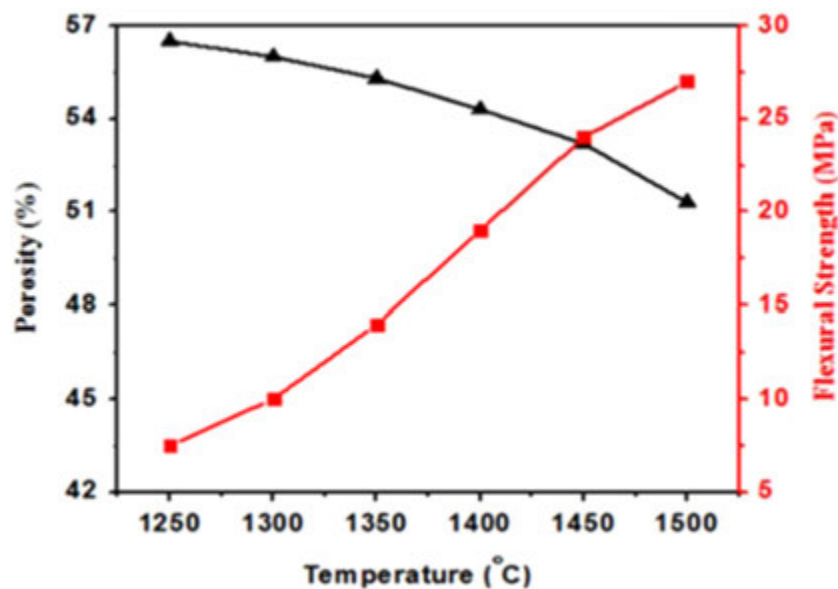


Fig. 14 Porosity and flexural strength of homogeneously sol-coated samples sintered at different temperatures [30].

% mullite sol coating content, the flexural strength is 24 MPa and the open porosity is 53%. There are two main methods used to enhance the mechanical properties and corrosion resistance. The first is that the apparent porosity decreases with increasing sintering temperature, with an increase in flexural strength (see Fig. 14).

The second is the transformation of the mullite precursor to a liquid binder, creating an interlocking structure at 1450°C, which leads to improvements in the thermal alkali resistance and the mechanical properties. In addition, the flexural strength is basically affected by the microcracks, the porosity and the bonding necks between the particles, and thus the porous ceramics possess a higher flexural strength due to their bending fewer microcracks, a lower porosity and thicker necks. The porous mullite ceramic reinforcement is attributed to the condensation reactions and mechanisms of thermal activation that lead to an increase in the connectivity of the mullite gel network, as in Fig. 15(a) and (b). This homogenous structure improved the flexural strength effectively and could be attributed to the unique crystal structure of mullite. The pore size of porous mullite ceramics about (80–100 μm) is suitable to filter impurities such as in industrial hot exhaust gases [30].

Benhammoua *et al.* [31] studied the effect of the sintering cycle (conventional and three steps sintering) on the microstructure and mechanical properties of porous cordierite ceramics using oil shale (OS) as a pore forming agent. The study showed that the conditions of sintering (conventional and three steps sintering) have a high impact on the mechanical properties of porous cordierite ceramics. Conventional sintering (CS) at 1300°C for 2 h at a temperature rate of 10°C/min resulted in an increase in open porosity from 17.7 to 52.8% and pore size, while sintering in three steps (heating up to 1350°C for 1 h as a soaking time and then heating at 750°C, followed by heating at 1300°C under the same conditions) led to higher tensile and flexural strengths of 16.8 and 25 MPa, respectively, compared to porous cordierite ceramics using CS (7.54–11.2 MPa). This enhancement in the mechanical properties using three-step sintering is due to the decrease in the pore size and porosity ratio, as in Fig. 16 [31].

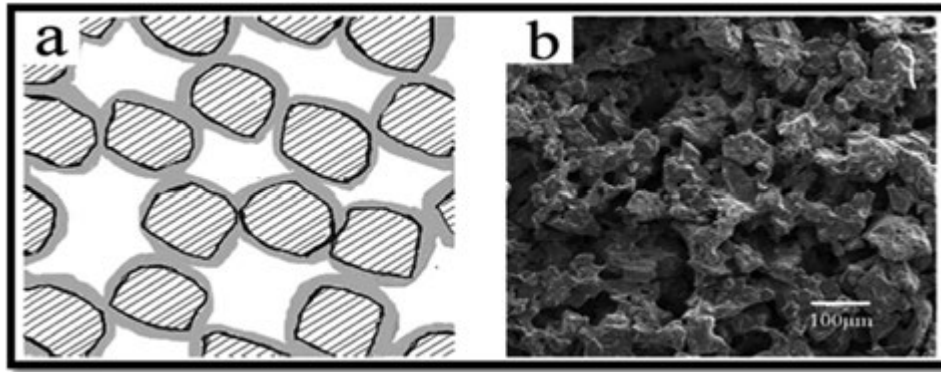


Fig. 15 (a) Microstructure schematic illustration of the sintered homogeneous sol-coated sample and (b) typical scanning electron microscope (SEM) micrograph of homogeneous sol-coated sample sintering at 1450°C [30].

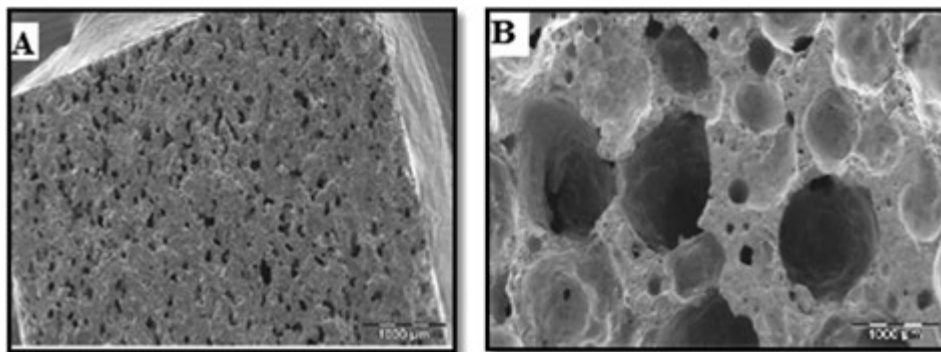


Fig. 16 (A) low pore size and porosity in the three-step sintering. (B) High pore size and porosity in the conventional cycle which affects the mechanical properties of porous ceramics [31].

Yin *et al.* [32] studied the effect of sintering temperature on the mechanical properties of porous Si_3N_4 ceramics used for heat exchanger applications using the protein foaming method. The results indicated that the compressive strengths of the porous Si_3N_4 ceramics increase with increasing sintering temperature from 12.85 MPa at 1750°C to 19.99 MPa at 1820°C because of the decrease of porosity from 86.42 to 83.32% with increasing sintering temperature. Donga *et al.* [33] studied the effect of sintering temperature and soaking time on the improvement of the mechanical properties of highly porous fibrous YSZ ceramics using the gel casting process and pressure less sintering. It is found that the mechanical strength of porous ceramics increases from 0.34 to 0.66 MPa when increasing the sintering temperature from 1500 to 1650°C and the porosity decreases from 90 to 86.6% with a mean pore size of 30.2 µm. Meanwhile, with a long soaking time, the change in porosity is not clear and the compressive strength increases gradually (see Fig. 17). The authors reported that the enhancement in the mechanical properties was attributed to the unique structure of the porous ceramics which have a bird's nest shape. This structure is a naturally designed structure with high strength and low porosity. Table 2 shows examples of sintering temperature effects on the mechanical properties of some porous ceramics materials with different work conditions as in studies conducted by various researchers.

Effects of Pore Forming Agent

This section, presents the effects of pore forming agent and porosity on the mechanical properties of porous ceramics materials. Huec *et al.* [34] studied the influence of porosity on the mechanical resistance of hydroxyapatite (HAP) ceramics under compressive stress. It is found that the total porous volume is in the range of 20–60% and the pore size ranges from 5 to 400 µm. Total porosity and pore size can influence compressive strength. With increasing porosity and pore size the compressive strength decreases. Liu *et al.* [35] studied the effect of pore size and porosity on the compressive strength of porous HAP ceramics using poly vinyl butyral (PVB) as a pore forming agent. The study showed that the porous (HAP) ceramics consisting of larger macro-pores exhibit lower strength in comparison with those of smaller macro-pores (see Fig. 18). The range of macro-pore sizes is from 93 to 420 µm while the range of porosity is from 33 to 78%. This range of pore size can be fabricated by controlling the starting size of PVB as a pore forming agent.

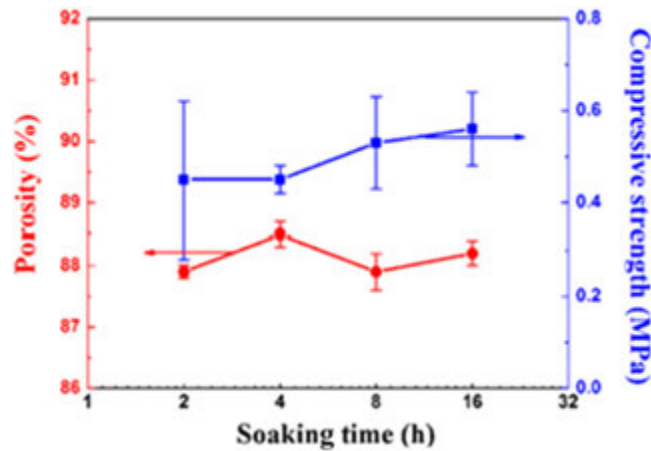


Fig. 17 Variation of porosity and compressive strength of fibrous Yttria-stabilized zirconia (YSZ) ceramics sintered at 1600°C with different soaking time [33].

The relationship between the compressive strength behavior of porous HAP and the porosity volume has been mentioned by many researchers. Using Rice's formula, the compressive strength correlated exponentially with the porosity volume equation.

$$\sigma = \sigma_0 e^{(-bp)} \quad (1)$$

where σ is the strength at pore volume fraction P , σ_0 is zero-porosity strength, and the constant b is related to the pore characteristics (see Fig. 19).

Yang *et al.* [36] presented the effects of pore morphology on the fabrication and mechanical properties of porous Si_3N_4 ceramics using organic whiskers to produce rod-shaped pores through the slip casting technique, and starch to produce equiaxial pores by the die press process (acting as a pore forming agent). It is found that the flexural strength decreases with increasing porosities, however, no difference in the flexural strength was exhibited for these two kinds of pore shape and the porosity increases with increasing pore agent content (see Fig. 20).

Ding *et al.* [37] reported the fabrication of mullite-bonded porous SiC ceramic using graphite as a pore former. The study showed that with increasing porosity the load-bearing area decreases when the porous SiC is fractured, that leading to a decrease in the flexural strength. Also, with high porosity, the porous ceramics fail suddenly at a stress that is far below the bulk material's strength. However, the failure is non-disastrous because the microcracks have been arrested by the pores. In addition, the local failure of a single strut does lead to whole material failure. Progressive fracture occurs when the load is transferred to the neighboring pores (see Fig. 21). Porous SiC ceramics with a lower porosity and more neck growth possess a larger minimum solid cross-sectional area and higher flexural strength.

In addition, the flexural strength is enhanced from ~5.1 to ~24.0 MPa when the sintering temperature is increased from 1400 to 1550°C. In subsequent mullitization, the crystallization of amorphous SiO_2 and the oxidation of SiC are increased with increasing sintering temperature. These changes lead to an increase in the neck area between the SiC particles. Additionally, more silica with a low viscosity, which is a result of the higher sintering temperature, leads to a reduction in the porosity of porous SiC ceramics. The flexural strength decreases suddenly with increasing graphite content and increases slightly with increasing forming pressure [37]. Eom *et al.* [38] reported the effect of using hollow microspheres as a sacrificial template on the mechanical properties of porous SiC ceramics using the carbothermal reduction of poly siloxane-derived SiOC. The study showed that the superior compressive and flexural strength of porous SiC ceramics were ~240 MPa and ~60 MPa, respectively with ~40% porosity. In general, the compressive and flexural strengths of SiC ceramics in the range of porosity 44–77% decrease with increasing porosity (see Fig. 22) [38].

Zhi-hua *et al.* [39] prepared a macro-porous bioactive glass ($\text{CaO-SiO}_2\text{-P}_2\text{O}_5$ system) using granular stearic acid as a pore former with the aid of the sol gel method. The study showed that the ranges of pore diameter that were created by the pore former were 100–300 μm , and the porosity and pore size can be controlled by the forming pressure. When increasing the forming pressure from 100 to 250 MPa, the compressive strength and porosity increase. The porosity and compressive strengths were 59.90% and 6.29 and 250 MPa, respectively. Yong *et al.* performed a comparison study for three types of carbon (C) sources (carbon black, phenol resin, and xylene) and (Si) silicone to fabricate porous SiC at a range of temperatures from 1700 to 1850°C. The study showed that the porous SiC ceramics produced using black carbon exhibit the best strength compared to the other sources of carbon [40,41]. Yoshida *et al.* [42] presented the effect of pore size on the fracture strength of porous alumina ceramics. It is found that with increasing pore size from 6 to 490 μm the fracture strength decreases from 63 to 20 MPa with equal amounts of porosities. In addition, the fracture energy increases with increasing pore size, which proves that the crack propagation behavior is affected by the pore size. Chae *et al.* studied the effect of template size and content on the porosity and strength of macro-porous zirconia ceramics. The study showed that with increasing template size at the same template content the porosity increased. The

Table 2 Examples of sintering temperature effects on the mechanical properties of some porous ceramic materials with different work conditions

Author	Work conditions							Major finding		
	Porous materials	Method	Range of sintering temperature (°C)	Range of pressure (MPa)	Mixing method	Pore forming ratio and particle size (%) and (μm)	Soaking time (h)	Pore size (μm)	Porosity ratio (%)	Mechanical properties
Donga <i>et al.</i>	Yttria-stabilized zirconia (YSZ) fibers as raw material diameter (1–10 μm)	Gel casting and pressureless sintering	1500–1650°C	–	Ball milling (30 min)	–	2–16 h	30.2	86.6–90.0%	Inspired by nest structure, fibers interconnect with good interfacial bonding on junctions. Under higher sintering temperature, porosity drops gradually while compressive strength increases significantly 0.34–0.66 MPa [33]
Benhammou <i>et al.</i>	Cordierite	Solid state reaction technique	Conventional sintering (CS) (1300°C)	120	Mixing by mortar	Oil shale (OS) (40 μm) – (10, 15, 20%)	2 h	CS (10–80)	17.7–52.8%	The maximum addition of OS and CS lead to increased porosity and pore size
			Three sintering steps (TSS) (350, 750, and 1300°C)				1, 1, and 2 h	TSS (50–80)		TSS presented higher tensile and flexural strengths (16.8 and 25.4 MPa, respectively), than those of porous ceramics sintered by CS cycle 7.54–11.2 MPa, respectively A significant decrease in flexural strength 44.67 ± 5.7 to 17.87 ± 2.8 MPa, tensile strength 19.147 ± 2.6 to 12.47 ± 1.5 MPa, and Young's modulus 70.57 ± 0.7 to 46.87 ± 0.2 GPa was observed with increasing OS addition from 0 to 20 wt% [31]
Wu <i>et al.</i>	Mullite	Sol gel-coated powder	1250–1500°C	–	Ultrasonic dispersion and stirring 10 h	Expandable polystyrene (EPS) microbeads (~100 μm) 50 vol%	–	–	53%	The porous mullite ceramics with 30 wt% mullite sol coating content that sintered at 1450°C showed an open porosity of 53% and flexural strength of about 24 MPa it is best performance point [30]
Chena and Miyamotoa	Silicon carbide (SiC)	A sintering-decarburization process (powder metallurgy)	Decarburized in air	30	–	Carbon (20 μm)	10 h	Large pores (20 μm)	66.7%	The porous ceramics made at 600°C has a bending strength of 23 MPa and compressive strength of 101 MPa. The porous SiC made at 1000°C has a bending strength of 26 MPa and compressive of 106 MPa [29]
			600°C 1000°C				5 h	Small pores (2.1 μm)	70%	
Kayal <i>et al.</i>	Mullite	Liquid precursor or infiltration	1300–1500°C	–	–	Petroleum coke powder ash (0–0.26 vol%)	4 h 4 h	–	31–48%	The flexural strength and the Young's modulus of the porous ceramics varied in the ranges of 19.3–43.8 MPa and 16.6–42.9 GPa, respectively and higher flexural strength and elastic modulus were achieved by increasing the sintering temperature of the ceramics [27]
Manoj <i>et al.</i>	Silicon carbide (SiC)	Powder metallurgy	1800–1950°C	50	Ball milling (3 h)	Polycarbosilane (PCS; type A) (0–50 wt%)	1 h	–	32–59%	Flexural strength from 16 to 96 MPa by controlling the filler type, filler content, and sintering temperature Porosity decreased and strength increased with increase in sintering temperature irrespective of the filler source and content [25]

(Continued)

Table 2 Continued

Author	Work conditions							Major finding		
	Porous materials	Method	Range of sintering temperature (°C)	Range of pressure (MPa)	Mixing method	Pore forming ratio and particle size (%) and (μm)	Soaking time (h)	Pore size (μm)	Porosity ratio (%)	Mechanical properties
Feng Ye <i>et al.</i>	Silicon nitride (Si ₃ N ₄)	Unidirectional freeze casting	1700–1900°C under a 0.1 MPa nitrogen atmosphere	–	Ball milling 20 h and stirring in a vacuum desiccator	–	1.5 h	–	72.1–73.2%	Flexural strength and fracture toughness are increased from 21 to 73 MPa and 0.5 to 1.1 MPa.m ^{1/2} , respectively with increasing sintering temperature [24]
Yan <i>et al.</i>	Corundum–mullite	Powder metallurgy	1300–1600°C	100	Ball milling 4 h	–	3 h	–	42–45%	The sintering temperature strongly affects the formation of secondary mullite, and then changes the pore characteristics and strength With high mullite content 86.6 wt%, high apparent porosity 42%, high crushing strength 52 MPa and a homogeneous pore size distribution at 1500°C [22]
Jin and Kim	SiC	Powder metallurgy	1100–1400°C in argon	50	Ball milling 6 h	Polymer microbeads 8 μm (40–90 wt %) as a template	1 h	–	40–90%	The typical flexural strengths of the porous ceramics pyrolyzed at 1400°C were ~30 MPa at 70% porosity and ~6 MPa at 80% porosity [21]
Lianfa Hu and Chang-An Wang	YSZ	Gel casting	1350, 1400, 1450, 1500, and 1550°C	–	Ball milling 5 h	Tert-butyl alcohol (TBA)	2 h	0.73–1.82 μm	65–77%	The compressive strength increased from 3 to 27 MPa with the increase of sintering temperature from 1350 to 1550°C [20]
Yu-Ping Zeng and Dongliang Jiang	SiC	Powder metallurgy	1350–1550°C	56	Ball milling 24 h (150 rpm)	Graphite 99% purity	2 h	10 μm	51.1% Without preheat-treated aluminosilicate (PHAS) 35.3–48.6% with PHAS	Flexural strength increases with increasing sintering temperature for both porous ceramics, with PHAS 21.5–86.9 MPa and without PHAS (14 MPa) [19]
Jeom <i>et al.</i>	SiC	Powder metallurgy (by carbothermal reduction and subsequent sintering)	1800–1950°C	27	–	Carbon-filled polysiloxane	1 h in nitrogen	(0.003–30 μm)	39–55%	Typical compressive and flexural strength values at ~40% porosity were ~290 and ~100 MPa, respectively, at 1950°C [18]
Chi <i>et al.</i>	SiC	Powder metallurgy	1100–1300°C	–	Ball milling (12 h) and blend (30 min) with pore agent	Yeast (350–450 μm)	1–5 h	(350–450 μm)	61.4–68.5%	Flexural strength increases in range of 7.6–16.8 MPa at holding time 3 h with increasing sintering temperature [17]
Carelli <i>et al.</i>	Mullite/alumina	Vacuum-infiltrated into a fiber cloths	100–1200°C	–	–	–	1000 h	–	37.7–38.3%	Increases the hardness, tensile strength and modulus of porous mullite/alumina ceramic composites which increases the aging time and sintering temperature [16]

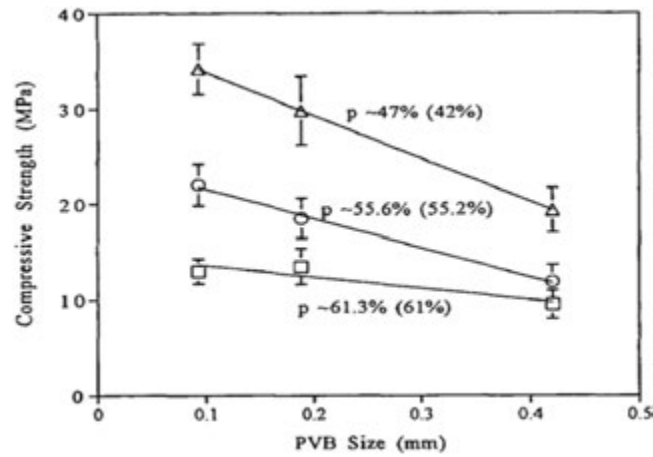


Fig. 18 Increasing macro-pore size, the compressive strength of porous (hydroxyapatite (HAP)) ceramics decreases linearly for a given total porosity [35].

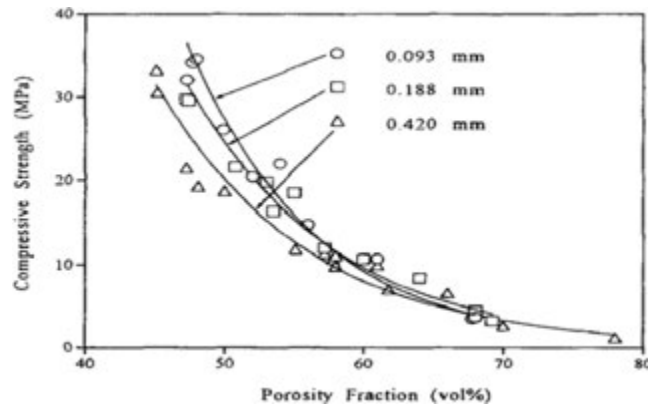


Fig. 19 Porosity and compressive strength behavior of porous hydroxyapatite (HAP) ceramics in different sizes of pore forming [35].

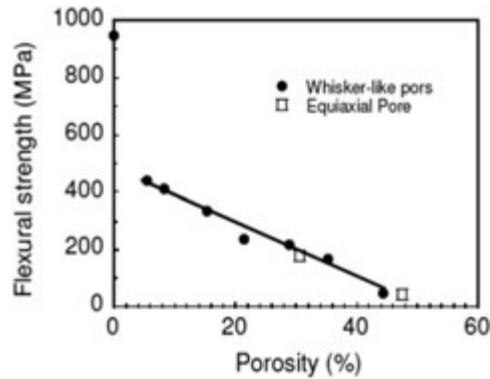


Fig. 20 Flexural strength as a function of porosity for porous silicon nitride (Si_3N_4) samples containing rod-shaped and equiaxial pores [36].

compressive and flexural strengths were primarily affected by the porosity rather than the template size, while through decreasing the template size at the same porosity, the strength increased. The excellent compressive and flexural strengths at 60% porosity were ~ 75 MPa and ~ 30 MPa, respectively. Controlling the content and the template size would enable the fabrication of macro-porous zirconia ceramics with porosities ranging from 58 to 75% [43,44]. Eom and Kim [45] presented the effect of template size (polymer microbeads) on the microstructure and strength of porous SiC ceramics using a sacrificial template process. It is found that both the compressive and flexural strengths increase with decreasing porosity and both the flexural and compressive strengths increase with decreasing template size, i.e., pore size, because of an increase in strut strength and a decrease in the critical flow size. The typical compressive and flexural strength are 600 and 105 MPa, respectively, at a porosity of 30%. Zhang and Ye [46] reported

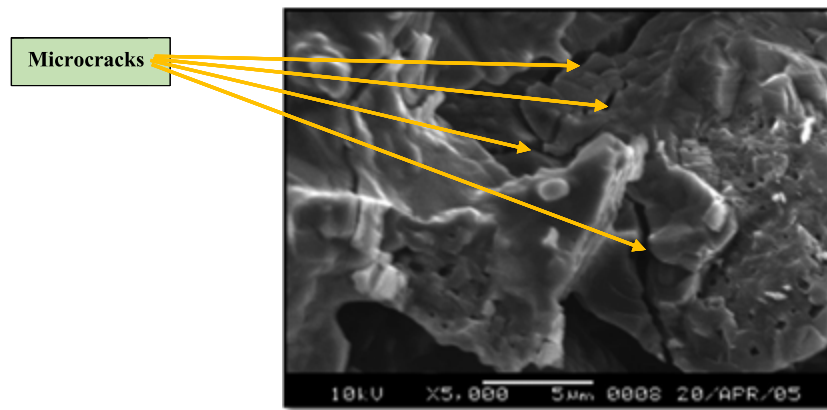


Fig. 21 Microcracks at the necks when porous silicon carbide (SiC) ceramics fractured [37].

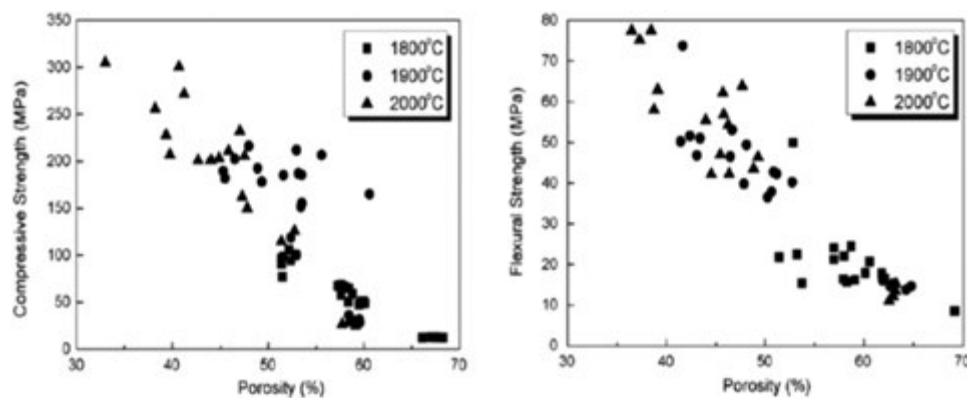


Fig. 22 Compressive and flexural strength of the porous silicon carbide (SiC) ceramics as a function of porosity [38].

on porous Si_3N_4 self-reinforced ceramics prepared by gel casting using agarose solutions. The study showed that the $\alpha \rightarrow \beta$ - Si_3N_4 phase transformation, the porosity and the mechanical properties were affected strongly by the agarous content solutions. When the agarose content changed from 0.2 to 0.8% (w/w based on powder), the fracture toughness decreased from 6.6 to 5.5 $\text{MPa}\cdot\text{m}^{1/2}$, while the fracture strength decreased from 455 to 316 MPa and the porosity increased from 10.3 to 21.4%. The porosity has the main effect on the mechanical properties of porous Si_3N_4 ceramics. Increases in the pore size and porosity lead to decreases in the fracture toughness and flexural strength. In addition, a suitable strength of interfacial bonding and the elongation of β - Si_3N_4 grains could contribute to a high fracture toughness by encouraging bridging and crack deflection (see Fig. 23).

Choi *et al.* [47] studied the effect of template content on the microstructure and flexural strength of porous mullite-bonded silicon carbide ceramics (MBSC). The study showed that by controlling the sintering temperature and the content of the template, porous mullite-bonded SiC with porosities in the range of 30 to 54% can be produced. Increasing the template content at a constant sintering temperature leads to an increase in porosity. The flexural strength after sintering at 1450°C for 2 h showed a maximum value due to the dense strut and small pores for porous ceramics and the maximum flexural strength was ~51 MPa at 30% porosity when no template was used at a sintering temperature of 1450°C for 2 h. Veljovic *et al.* [48] investigated the effect of pore shape and size on the mechanical properties of porous HAP-based bioceramics. It is found that through increasing the sintering temperature from 1100 to 1250°C, the number of shapeless inter-agglomerate pores decreases and the number of spherical pores increases, leading to an improvement in the fracture toughness ($1.31 \text{ MPa}\cdot\text{m}^{1/2}$) of porous HAP-based ceramics. They reported that this improvement in fracture toughness may be attributed to the formation of continuous necks between the strong spherical agglomerates. Fenga *et al.* [49] studied the effect of the addition of polyvinylpyrrolidone (PVP) as a pore forming agent and binder on the mechanical properties and porosity of porous alumina ceramics. The study indicated that both the pore morphology and the porosity affected the mechanical properties, when the porosity was in the range of 30–45%. Also, the porous alumina ceramics that were prepared using acetone as a solvent of PVP exhibited the highest Young's modulus (57.4 GPa) and bending strength (140.2 MPa) because of the cylindrical pores that were aligned to some extent, which were 3.4 times and 1.6 times higher compared to those manufactured without PVP. The use of PVP during wet ball milling leads to a more uniform dispersion of the PVP alumina, which helps in increasing the bonding of the grains and limiting the growth of grains during the sintering process. Hence, this will lead to an increase in the toughness of porous alumina ceramics. Fukushima *et al.* [50] used ice crystals as a pore forming agent to prepare macro-porous SiC ceramics using gelation freezing and partial sintering. The results

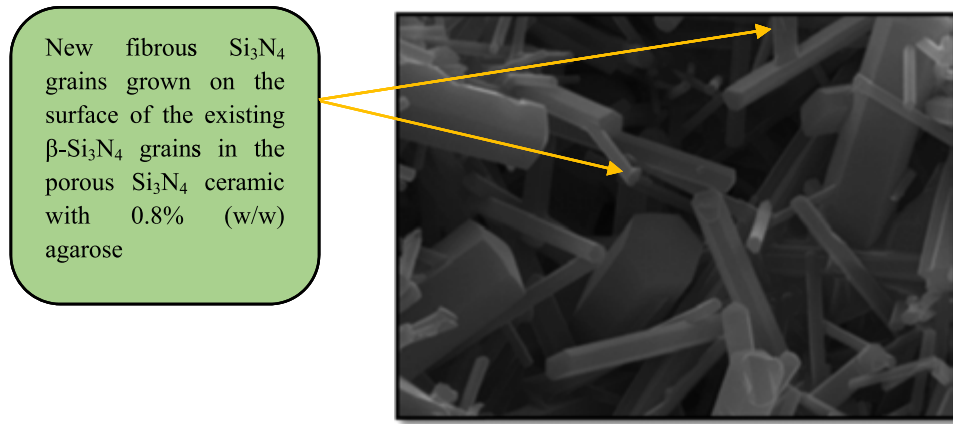


Fig. 23 Morphology of fracture of porous silicon nitride (Si_3N_4) ceramics [46].

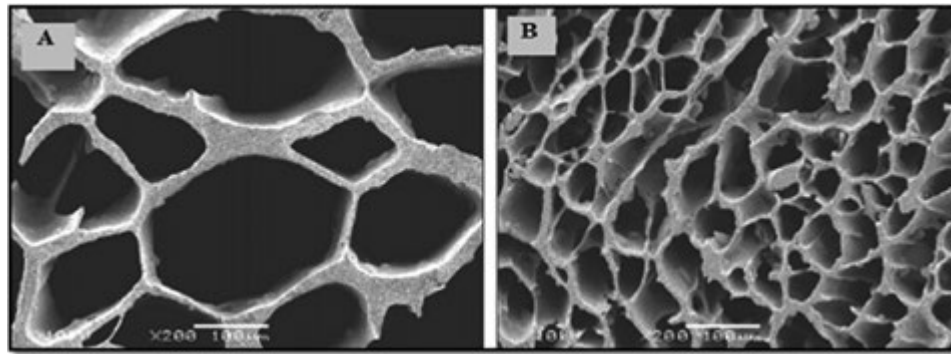


Fig. 24 (A) and (B) unique honeycomb morphology for porous silicon carbide (SiC) fabricated using the gelation freezing method [50].

revealed that the compressive strength of porous SiC is in the range of 5.2–16.6 MPa and the porosity is in the range of 30–90% when using a gelation freezing route. Depending on the cell size, where the load was parallel to the cell (freezing direction), it has been shown by other researchers that the compressive strength of porous SiC prepared by other methods (partial sintering) was ~ 10 MPa with 70% porosity and a cell size of 20–47 μm , and 16.7 MPa with 80% porosity and a cell size of 20–100 μm . Meanwhile, the compressive strength of porous SiC ceramic using gelation freezing was 16.6 MPa at a porosity of 90% and a cell size of around 30–150 μm . The microstructure of porous SiC fabricated using the gelation freezing method consisted of a unique honeycomb with a 3D interconnected pore network, which gives excellent compressive strength to porous SiC ceramics compared to other methods, for example, the partial sintering method (see Fig. 24).

Sengphet *et al.* [51] reported that kenaf powder (KP) waste can be used to fabricate porous clay ceramics, acting as a pore forming agent. The study showed that with increasing organic content (KP) in porous clay ceramics the density decreased from 1.75 to 1.3 g/cm^3 , the porosity increased from 11.86 to 45.64% and the shrinkage was between 11.72 and 15.9%. Meanwhile, the tensile strength decreased from 24.05 to 9.06 MPa as shown in Fig. 25. The decrease in the tensile strength of porous clay ceramics is attributed to the increase in porosity, which is generated by the decomposition of the organic materials from the KP waste during the sintering process of porous clay ceramics.

Mohanta *et al.* [52] studied the effect of rice husk as a pore-forming agent on the mechanical properties of porous alumina ceramics. The study showed that through increasing the ratio and the size of the rice husk powder, the porosity increased while the mechanical properties decreased. This can be understood because the mechanical properties and the porosity are normally inversely related. The porous alumina ceramics with hardness of 149–18 HRD, modulus of elasticity between 250–18 GPa, porosity of 20–66 vol%, pore size of 50–516 μm and flexural strength of 22.3–207.6 MPa are as shown in Fig. 26.

Benhammoua *et al.* [31] studied the effect of OS as a pore former on the mechanical properties of porous cordierite ceramics. The results revealed that with the addition of OS from 0 to 20%, a significant decrease in the mechanical properties occurred: the Young's modulus decreased from 70.5 ± 0.7 to 46.8 ± 0.2 GPa, the tensile strength decreased from 19.147 ± 2 to 12.47 ± 1.5 and the flexural strength decreased from 44.6 ± 5.7 to 17.87 ± 2.8 MPa. The decrease in the Young's modulus and the flexural strength with increasing porosity can be attributed to the following Rice's models, respectively:

$$E_p = E_0 \exp(-bp) \quad (2)$$

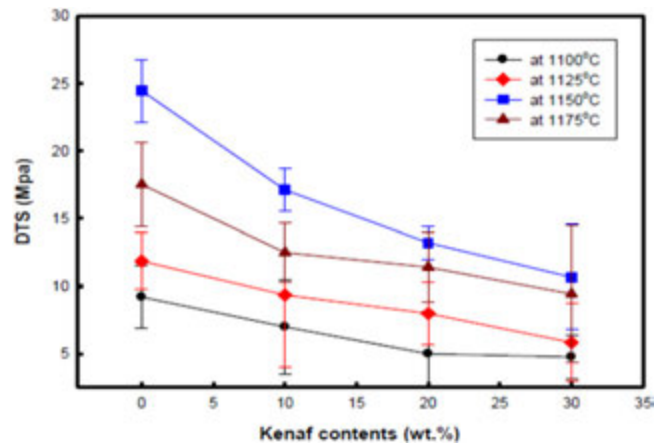


Fig. 25 Decreasing diametric tensile strength (DTS) of the porous clay ceramics with increasing kenaf content ratio at different sintering temperatures [51].

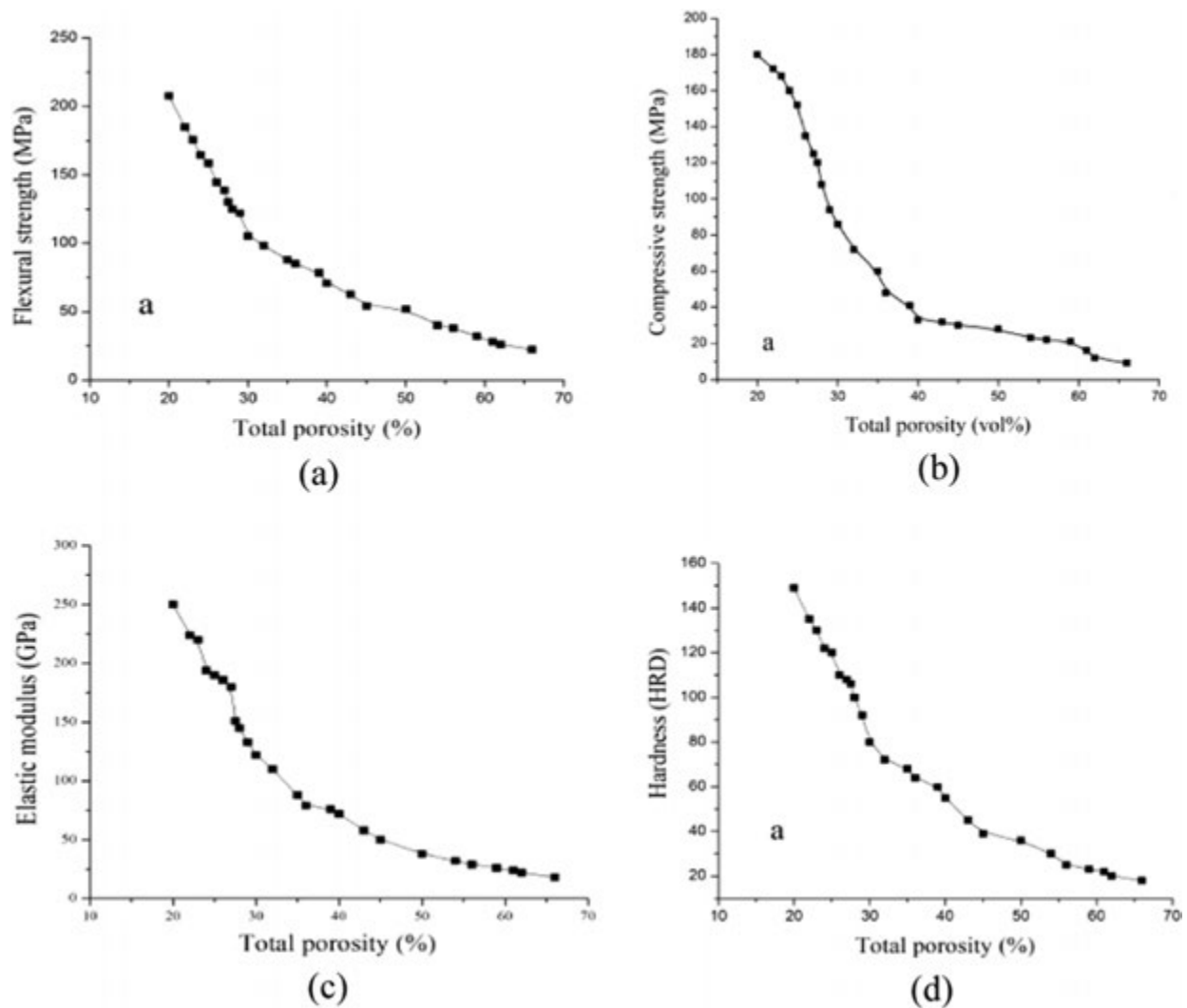


Fig. 26 Decreasing of the mechanical properties ((a)-flexural, (b)-compressive, (c)-elastic modulus and, (d)-hardness) for porous alumina ceramics with increases in the porosity using rice husk as a pore forming agent [52].

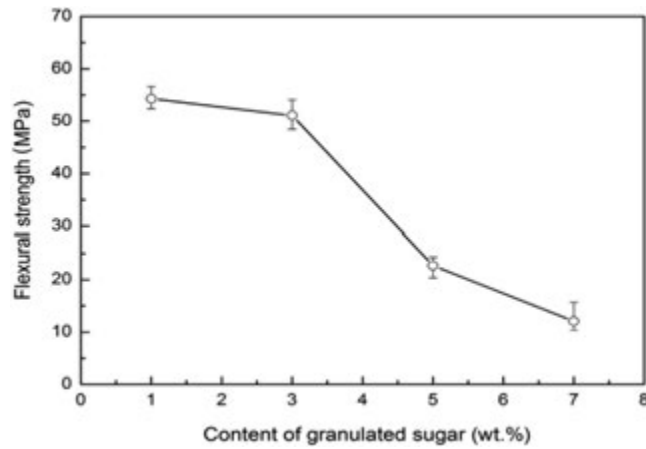


Fig. 27 Effects of granulated sugar content on the flexural strength of vitrified bond cubic boron nitride (CBN) grinding wheels [55].

$$\sigma_p = \sigma_0 \exp(-mp) \quad (3)$$

where E_0 and σ_0 are respectively the Young's modulus and the flexural strength of the pore free materials, P is the volume fraction of the pores and m , b are empirical constants. Novaïn *et al.* [54] studied the effect of polypropylene (PP) and poly methyl-methacrylate (PMMA) as a pore former with particle sizes of 250–425 μm on the mechanical properties of porous tile ceramics. The study showed that a significant decrease in the Young's modulus and the bending strength were obtained with an increasing level of porosity and pore forming agent content. By using PMMA as a pore forming agent at a particle size of 250 μm and ratios of 2.5–15 wt%, the bending strength and the Young's modulus were 86.5–54.7 MPa and 6.2–2.5 GPa, respectively. Also using PP as a pore forming agent resulted in marked decrease in the mechanical properties of porous tiles ceramics. Mao *et al.* [55] reported the effect of granulated sugar as a pore former on the microstructure and mechanical properties of the vitrified bond cubic boron nitride (CBN) grinding wheels as a glass system. The study showed that through increasing the granulated sugar content from 1 to 7 wt%, and a particle size of 160 μm , the porosity of the porous (CBN) wheel was in the range of 23.8–43.2%. The flexural strength of the porous CBN wheel decreases with an increase in the content of pore forming agent, as shown in Fig. 27. In addition, the content of pore forming agent not only affects the porosity, but also the size, shape, channels, and pore distribution. The flexural strength reaches 49 MPa when increasing the particle size of granulated sugar with a content of 3% when the particle size is 250 μm . Table 3 shows examples of the pore agent's effects on the mechanical properties for some porous ceramic materials.

Effects of Ceramic Additives

Ceramic additives have been used to improve the mechanical properties of porous ceramics. Many studies have been performed to determine the effect of ceramic additives on the ceramic's properties.

Guanghai Li *et al.* [56] studied the effect of nanoparticle addition on the mechanical properties of porous alumina ceramics. The study showed that the nano- Al_2O_3 can increase the thermal shock resistance, fracture toughness, and strength of the porous Al_2O_3 ceramics. Meanwhile, the Young's modulus of the porous alumina undergoes a marked increase after sintering at low temperature. The authors reported that the increases in the mechanical properties were attributed to the growth of the interparticle contacts by surface diffusion. The fracture toughness and the flexural strength of porous alumina ceramics increase with increasing ratio of nano- Al_2O_3 because of the accumulation of nanoparticles at the grain boundaries in conventional Al_2O_3 ; this leads to an improvement in the surface diffusion, hence increasing the growth of the contacts of the interparticle because of the high diffusion rate of the nanoparticles (see Fig. 28).

Lee *et al.* [57] studied the improvement in strength of porous SiC ceramics for hot gas filters and porous nickel oxide (NiO)-anode ceramics by controlling the additives (clay, alumina, mullite, Y_2O_3 , ZrO_2 , and calcium carbonate (CaCO_3)). It is found that the strength of the porous SiC and NiO-ceramics improves with the control of the additives. They reported that this enhancement in the strength of porous ceramics could be attributed to the bonded force between the grain and the neighboring grain without affecting the porosity much (see Fig. 29).

Yang *et al.* [58] studied the effect of adding a low content of Y_2O_3 as a sintering additive on the mechanical properties of porous β -SiAlON ($\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, $z=0.5$) ceramics. The results revealed that the porosity of porous SiAlON ceramics is in the range of 30–50% and there is a significant improvement in the mechanical properties (such as the flexural strength) with the addition of a low content of Y_2O_3 . They mention that the improvement in the flexural strength of the porous ceramics is attributed to the promoted grain bonding through the liquid-phase sintering with the addition of Y_2O_3 . In general, sintering additives strongly affect the sintering of SiAlON and SiC ceramics, and these sintering additives encourage phase transformation and densification. Therefore, the flexural strength of porous β -SiAlON ceramics was almost twice that of the porous β -SiAlON ceramics without the Y_2O_3 additives (see Fig. 30).

Table 3 Examples of pore agent effects on the mechanical properties of some porous ceramic materials with different work conditions

Author	Work conditions							Major finding		
	Porous materials	Method	Range of sintering temperature (final sintering)	Range of pressure (MPa)	Mixing method	Pore forming ratio and particle size (%) and (μm)	Soaking time	Pore size (μm)	Porosity ratio	Mechanical properties
Mao <i>et al.</i>	Boron nitride	Powder metallurgy	650 and 850°C At same sintering	–	Ball milling	Sugar (1–7%) (100–500 μm)	1 and 4 h At same sintering	100–500	23.8–43.2%	The porosity of the sintered specimens increases with increasing content of granulated sugar The flexural strength of the vitrified bond CBN wheel specimens decreases 51–22 MPa with an increase in pore former content and porosity [55]
Novaisn <i>et al.</i>	Porcelain	Powder metallurgy	500°C	–	–	Poly methyl methacrylate (PMMA; 2.5–15 wt%) 250–425 PP/ 2.5–15 wt%	15 min	–	PMMA (11.51–27.79%) Polypropylene PP (12.67–30.56)	Flexural strength decreases with increasing porosity and pore agent content for PMMA from 77.2 to 59.9 MPa and for PP from 87.9 to 58.9 MPa [54]
Mohanta <i>et al.</i>	Alumina	Powder metallurgy	1700°C	100	Mortar (30 min)	Rice husk ash (5–30 wt%) 75–600 μm	2 h	50–516	20–66%	Decrease in the mechanical properties such as flexural strength of 207.6–22.3 MPa, compressive strength of 180–9.18 MPa, elastic modulus of 250–18 GPa, and hardness of 149–18 HRD with increasing porosity [52]
Sengphet <i>et al.</i>	Clay	Powder metallurgy	1100–1175°C	–	–	Kenaf (0–30 wt %) 75–600	3 h	500	11.86–45.64%	With increase in porosity, the tensile strength was in the range of 9.06–24.05 MPa With increase in porosity, shrinkage is between 11.72 and 15.90% [51]
Fukushima <i>et al.</i>	Silicon carbide (SiC)	Partial sintering Sacrificial pore formers (casting)	1500–1800°C 1800°C	CIP 100 CIP 400 –	Planetary ball mill (1 h) Ball milling	– Ice crystals	2 h 2 h	0.03–0.70 30–150	30–90%	In partial sintering, compressive strength is ~ 10 MPa with 70% porosity and cell size of 20–47 μm and 16.7 MPa with 80% porosity While the compressive strength is in the range of 5.2–16.6 MPa and the porosity is in the range of 30–90% using the gelation freezing route [50]
Fenga <i>et al.</i>	Alumina	Powder metallurgy	1500°C	20	Ball milling (48 h)	Poly-vinylpyrrolidone (PVP)	10 h	–	30–45%	Both porosity and pore morphology affected by the mechanical properties [49]
Zhang and Feng	Silicon nitride (Si_3N_4)	Gel casting	1800°C Under 0.1 MPa nitrogen	–	Ball milling (24 h)	Agarose (0.2–0.8 wt%)	1.5 h	–	10.3–21.4%	The porosities increased from 10.3 to 21.4%, while the fracture strength decreased from 455 to 316 MPa and the fracture toughness decreased from 6.6 to 5.5 $\text{MPa}\cdot\text{m}^{1/2}$ [46]
Zhou <i>et al.</i>	Bioactive glass	Powder metallurgy	1200°C	100–250	Grinding (8 h)	Stearic acid as a (150–350 μm)	–	100–300 μm	56.81–59.9%	The compressive strength varied from 3.68 to 6.29 MPa [39]
Eoma <i>et al.</i>	SiC	Sacrificial templates	1800–2000°C	28	–	Hollow microspheres	–	–	44–77%	Compressive and flexural strength decreased with increasing porosity [38]
Ding <i>et al.</i>	Mullite-bonded porous SiC	Powder metallurgy (in situ reaction bonding technique)	1400–1550°C	30	Ball milling (24 h)	Graphite (5–20 μm)	4 h	1.6	38–56.6%	The open porosity decreases with sintering temperature and forming pressure, but increase with graphite content The increase in the porosity reduces the load-bearing area when porous SiC ceramics are fractured, which results in the decrease of the flexural strength [37]

Yang <i>et al.</i>	Si ₃ N ₄	Slip casting and die-pressing	1850°C under nitrogen gas (0.63 MPa)	CIP 150	Ball milling 24 h	Organic whiskers 33 μm, length of 300 μm (0–60 vol%) Potato starch 50 μm	4 h	–	45%	Porosity of the porous Si ₃ N ₄ ceramics was closely related to the agent contents, and high content led to high porosity The strength decreased considerably when a small amount of whiskers with rod-shaped pores, and starch with equiaxial pores were added [36]
Liu <i>et al.</i>	Hydroxyapatite (HAP)	Powder metallurgy	1200°C	27	–	Poly vinyl butyral (PVB) (93, 188, and 420 μm)	1–48 h	93–420	33–78%	The compressive strength behavior of the porous HAP can be correlated exponentially with porosity volume The porous HAP consisting of smaller macro-pore exhibits higher strength in comparison with those of larger macro-pores [35]
Huec <i>et al.</i>	HAP	Powder metallurgy	Above 1000°C	–	–	–	–	5–400	20–60%	This study confirms the decrease in compressive strength with increased porosity of HAP ceramics [34]

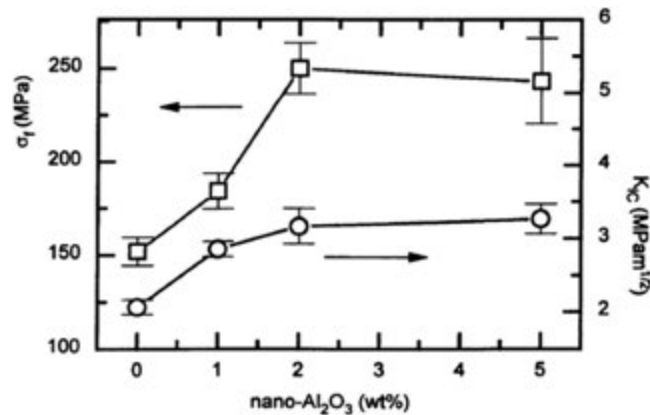


Fig. 28 Influence of nano-Al₂O₃ additions on the bending strength (σ_f) and the fracture toughness of the porous Al₂O₃ ceramics [56].

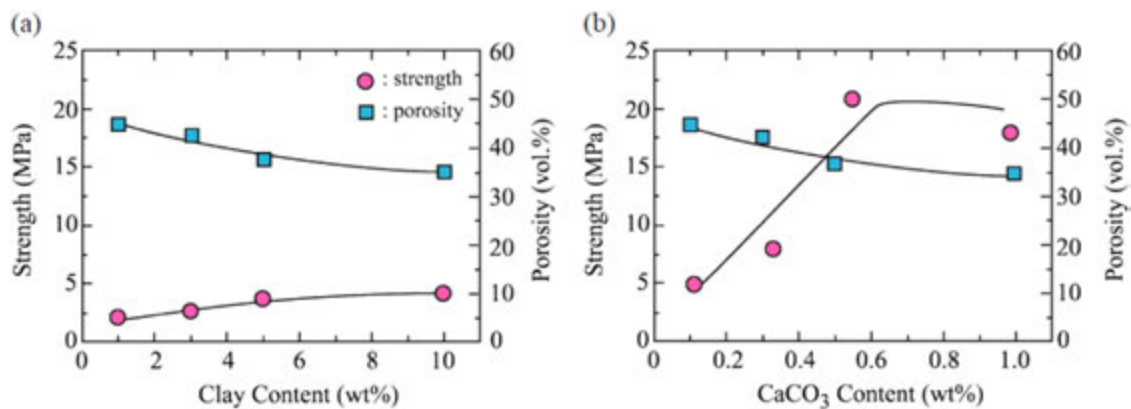


Fig. 29 Strength and porosity of silicon carbide (SiC) hot gas filter with (a) only clay additive and (b) clay 5 wt% + calcium carbonate (CaCO₃) additives. Circular points correspond to strength and rectangular points are for porosity [57].

Kord *et al.* [59] reported the effect of ZrO₂ addition on the mechanical-chemical, porosity, and crystallization behavior of CaO–TiO₂–P₂O₅ microporous glass ceramics. The study showed that with the addition of ZrO₂ the specific surface area increases, while the mean pore diameter and volume porosity were decreased. The largest surface area is 32 m²/g and the smallest median pore diameter is 8.6 nm for the porous glass ceramics of 6 mol% ZrO₂, which leads to a doubling of the strength of the porous glass ceramics from 15 ± 2 to 32 ± 3 MPa. Eom and Kim [60] reported the effect of sintering additives (Al₂O₃, Y₂O₃, Y₃Al₅O₁₂, MgO, SiO₂, CaO, and AlN) on the microstructure and strength of porous SiC ceramics fabricated by the carbothermal reduction of a polysilox-derived SiOC process. The results revealed that after sintering at 1750°C, the porosities of porous SiC ceramics are in the range of 56–72%, depending on the composition of the sintering additives. The highest strength of porous SiC ceramics with sintering additive ratios 2% AlN + 3% Y₂O₃ is 34 MPa at a porosity of 56%. They reported that this higher strength may be attributed to good sinterability, which could result in decreased porosity, and hence high strength porous SiC ceramics. In addition, inert fillers play a significant role in improving the strength and the control of dimensions during the processing of porous SiC ceramics by the carbothermal reduction process [61]. Gaiye *et al.* [62] studied the effect of YSZ (ZrO₂ stabilized by 3 mol% Y₂O₃) addition on the mechanical properties of macro-porous alumina ceramics. The study showed the preparation of macro-porous alumina ceramics with high mechanical properties by adding YSZ powder, and this powder plays a significant role in the improvement of the mechanical properties of macro-porous alumina ceramics. When the YSZ ratio is 6 wt%, the maximum value of fracture toughness is 3.0 MPa·m^{1/2} and the bending strength is 90 MPa. Also at 2 wt% YSZ, the maximum bending strength is 140 MPa (see Fig. 31).

They mentioned that the unique microstructure is useful for producing enhancements in the bending strength and fracture toughness of macro-porous alumina ceramics as shown in Fig. 32. This figure shows the important factors that lead to improvements in the mechanical properties; the first is the uniform dispersion of the YSZ particles in the framework of the alumina coarse particles, and the second is the “sandwich structure” which has been formed due to some of the YSZ particles becoming partially embedded between the alumina particles in the cooling stage (see Fig. 32, points A, B, and C). This enhances the compact area among the alumina particles and blocks the crack path. Thirdly, the addition of YSZ particles can improve the surface diffusion, which leads to the formation of the bonding neck to obtain the best mechanical properties [62].

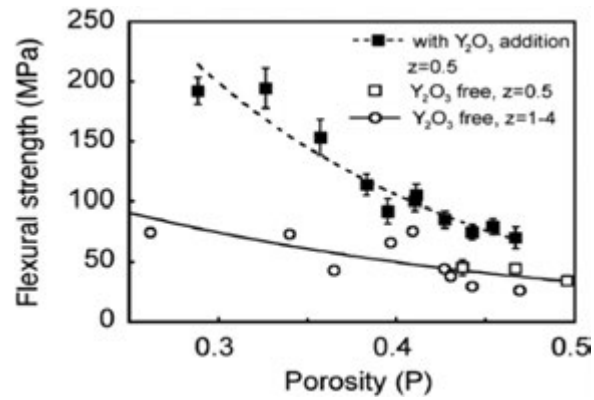


Fig. 30 Flexural strength as a function of porosity for the porous β -SiAlON ceramics [58].

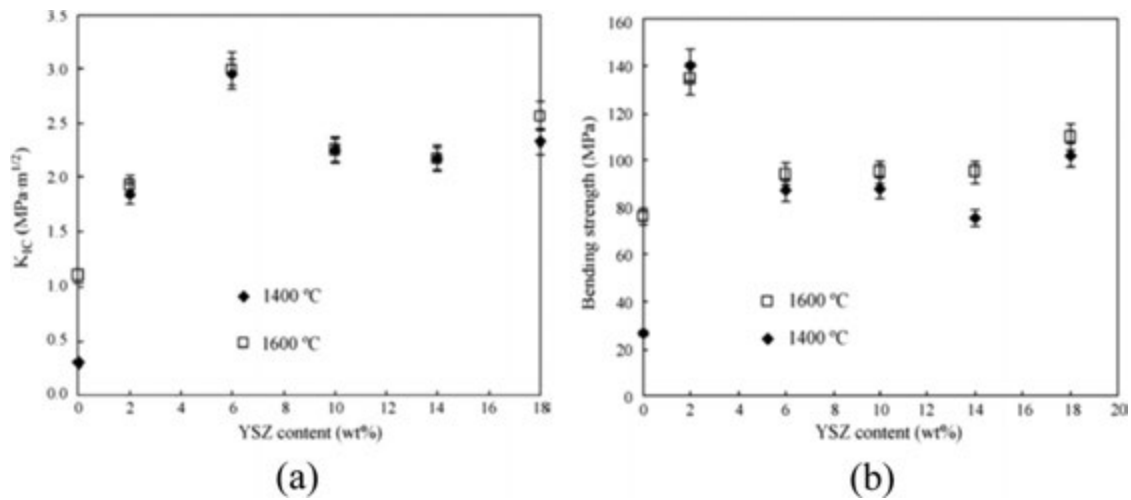


Fig. 31 Relationship between (a) fracture toughness and (b) bending strength of supports with yttria-stabilized zirconia (YSZ) content sintered at 1400 and 1600°C for porous alumina ceramics [62].

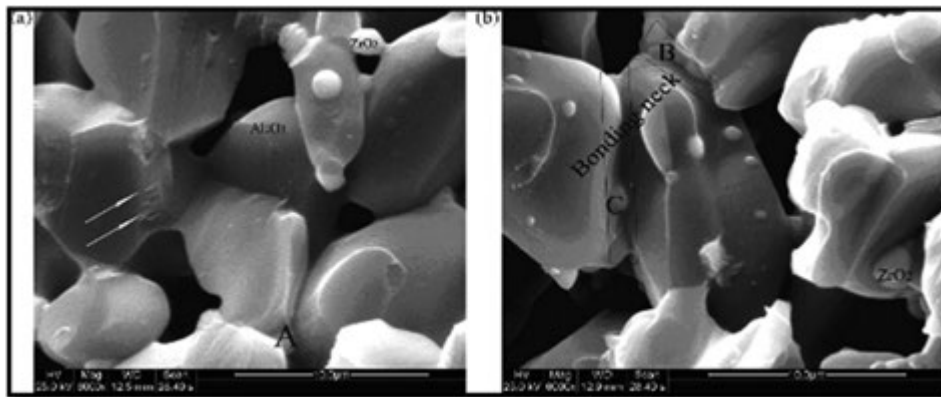
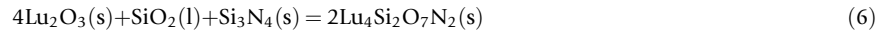


Fig. 32 Unique alumina microstructure reinforced by adding (a) 2 wt% and (b) 6 wt% yttria-stabilized zirconia (YSZ) powders sintered at 1600°C [62].

Rat'ko *et al.* [63] reported the influence of ceramic binders (sodium aluminosilicate, sodium aluminate, and sodium silicate) on the mechanical and structural properties of porous silicate ceramics. It is found that the sodium aluminosilicate additives have a strong effect on the mechanical properties. The porosity and compressive strength for sodium aluminosilicate, sodium aluminate, and sodium silicate are 34 vol%, 35 MPa; 37 vol%, 6 MPa; and 33 vol%, 18 MPa; respectively. This excellent compressive strength of porous silicate with sodium aluminosilicate compared to other additives, may be attributed to the structuration mechanism,

which leads to the formation of crystalline silica and the aluminosilicate binder. Lil *et al.* [64] studied the effect of hexagonal boron nitride (BN) on the mechanical properties and microstructure of porous Si_3N_4 ceramics. The study showed that through increasing the BN content in different ratio (25, 35, and 45 vol%), the porosity increases in the range of 17.8–30.4%, while the mechanical properties decreased from 210 to 105 MPa and from 3.4 to 1.9 $\text{MPa}\cdot\text{m}^{1/2}$ for the flexural strength and fracture toughness, respectively. Therefore the machinability improved. Wang *et al.* also found that the machinability of the dried green bodies of porous Si_3N_4 ceramics is excellent at 10 vol% BN additives [65,66]. Li and Yin [67] studied the effect of phase composition on the microstructure and mechanical properties of Lu_2O_3 -doped porous Si_3N_4 ceramics by adding SiO_2 as a ceramic additive to improve the mechanical properties of porous Si_3N_4 ceramics. It is found that the large ratio of SiO_2 leads to the formation of the secondary phase of $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\text{Si}_2\text{N}_2\text{O}$, while the small ratio of SiO_2 leads to the formation of the secondary phase of $\text{Lu}_4\text{Si}_2\text{O}_7\text{N}_2$. Porous Si_3N_4 with secondary phase $\text{Si}_2\text{N}_2\text{O}$ has a lower flexural strength, while with secondary phase $\text{Lu}_4\text{Si}_2\text{O}_7\text{N}_2$ it has a flexural strength of 207 MPa according to Eqs. (4)–(6).



Yu *et al.* [2] reported the effect of the β - Si_3N_4 additive on the mechanical properties and microstructure of porous Si_3N_4 ceramics. The study indicates that with increasing β - Si_3N_4 content in porous Si_3N_4 ceramics, the mechanical properties increase. By adding 3 wt% β - Si_3N_4 , this would result in a porosity of 44% and good mechanical properties. In addition, during the sintering process, there is a full transformation from α - Si_3N_4 to β - Si_3N_4 by the solution process with an hexagonal rod morphology (see Fig. 33), leading to the formation of interlocking microstructure and excellent mechanical properties attribute to this interlocking microstructure. Increasing the ratio of β - Si_3N_4 improved the flexural strength.

Wei *et al.* [68] reported the effect of La_2O_3 on the performance and preparation of porous cordierite from rice husk. The study showed that with the addition of 0–5 wt% La_2O_3 to porous cordierite ceramics, the mechanical properties greatly improved. The flexural strength improved from 4.42 MPa without using La_2O_3 to 11.38 MPa at 5 wt% of La_2O_3 , while the porosity exhibited a slight increase in the range of 42.40–45.02%. This means that the mechanical properties of porous cordierite were enhanced without decreasing the porosity. However, usually the mechanical properties of porous ceramics decrease with increased porosity. In this case, they reported that the increase in the mechanical properties and porosity may result from the effect of “spot welding” (see Fig. 34). During the sintering process of the porous ceramics, La_2O_3 additives produced liquids located between the grains and these solidify during cooling resulting in the strong bonding of these grains. In other words, the porous cordierite ceramics containing La_2O_3 not only obtain a suitable flexural strength but also high porosity. Fig. 34 shows the “spot welding” morphologies. At the junction of the cordierite particles, it can be observed that some neck-like connectors have formed. These connectors lead to bonding the cordierite particles together and improving the mechanical properties after sintering.

Choi *et al.* [69] reported the effect of alkaline earth metal oxide addition (CaO, SrO, and MgO) on the flexural strength of porous mullite-bonded SiC ceramics. It is found that the flexural strength of porous SiC ceramics increases with the addition of alkaline earth metal oxides; the flexural strength for porous SiC ceramics with Sr, Ca, and Mg additives are 44 MPa in porosity 46%, 29 MPa in porosity 44% and 18 MPa in porosity 47%, respectively, compared with a flexural strength 6 MPa in porosity 49% of porous ceramics without alkaline earth metal oxides. This improvement in the flexural strength may be attributed to mullite formation and the densification of porous ceramics with alkaline earth metal oxides. Li *et al.* [70] reported another way to improve the mechanical and dielectric properties of porous ceramics known as chemical vapor deposition (CVD), using three types of ceramic coatings (Si_3N_4 , BN, and boron carbide (B_4C)) for porous Si_3N_4 ceramics. This means that there is an improvement in the mechanical properties of porous ceramic by ceramic coating. The study showed after the CVD process, the Si_3N_4 - Si_3N_4 increased the flexural strength from 250 to 284 MPa and the Vickers hardness from 4.0 to 10.1 GPa as the deposition amount of Si_3N_4 increases from 7.9 to 29.4 vol%. The Si_3N_4 -BN increased the flexural strength from 217 to 221 MPa and the Vickers hardness from 2.1 to 2.9 GPa as the deposition amount of BN increases from 12.5 to 21.3 vol%; and the Si_3N_4 - B_4C increased the flexural strength

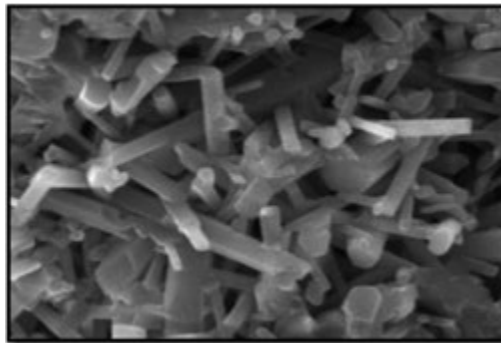


Fig. 33 Interlocking microstructure of β -silicon nitride (Si_3N_4) [2].

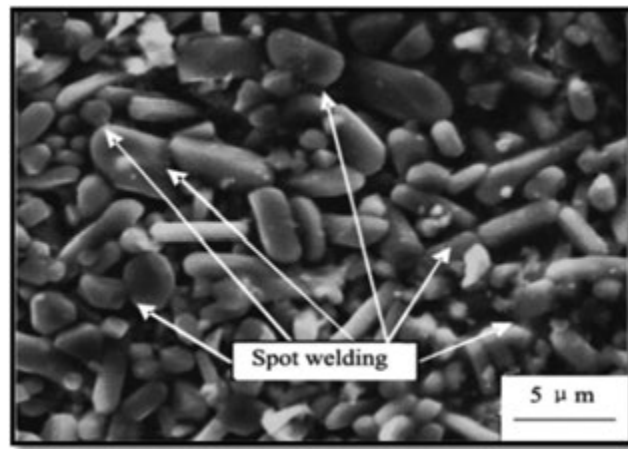


Fig. 34 Spot welding in microstructure of porous cordierite ceramics [68].

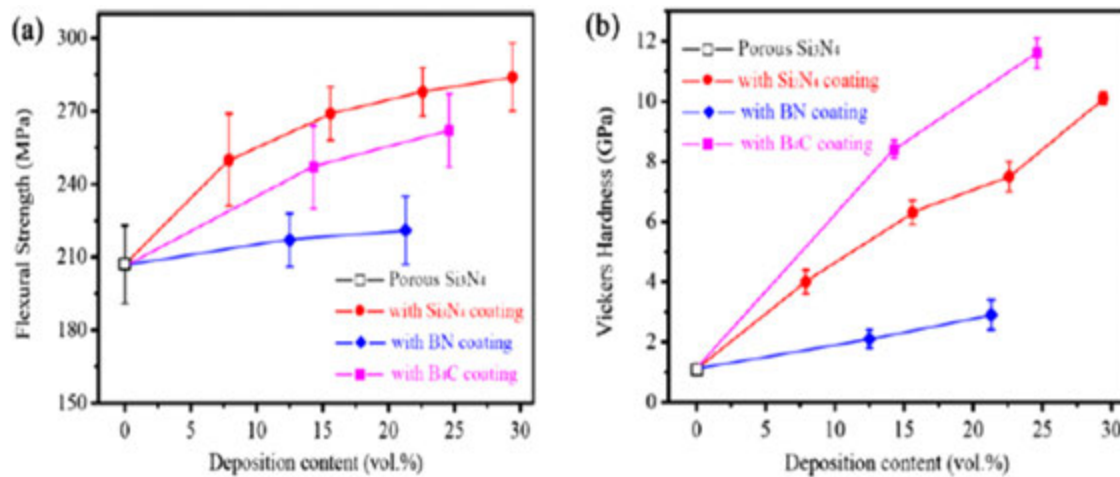


Fig. 35 (a) Flexural strength and (b) Vickers hardness of porous silicon nitride (Si₃N₄) ceramic, Si₃N₄-Si₃N₄, Si₃N₄-boron nitride (BN), and Si₃N₄-boron carbide (B₄C) [70].

from 247 to 262 MPa and the Vickers hardness from 8.4 to 11.6 GPa as the deposition amount of B₄C increases from 14.3 to 24.6 vol%. In other words, the CVD coating process, especially for B₄C and Si₃N₄, can improve the mechanical properties of porous Si₃N₄ significantly, leading to the enhanced mechanical erosion resistance of porous Si₃N₄ (see Fig. 35).

Feng *et al.* [26] studied the effect of ceramic binder addition on the mechanical properties of porous SiC ceramics. The study showed that through increasing the ceramic binder ratio, the porosity of porous SiC decreased, and hence the mechanical properties improved as shown in Fig. 36.

Yao *et al.* [71] studied the effect of BN addition on the mechanical properties of porous Si₃N₄/BN ceramic prepared by the nitridation of silicon powder. The study showed that when the porosity increased, both the fracture toughness and the Young's modulus of porous Si₃N₄/BN ceramics decreased with increasing BN ratio, while the flexural strength was significantly enhanced with 5% BN due to the interlocking morphology that favored crack bridging. Meanwhile, a decrease in the pore size with 5% BN influences the enhancement of the flexural strength of porous Si₃N₄/BN ceramics (see Fig. 37). In addition, the flexural strength of porous Si₃N₄/BN ceramics decreased with a high ratio of BN due to the interlocking of β -Si₃N₄ being prevented.

Kumar *et al.* [72] reported the improvement in flexural strength of porous mullite-bonded SiC ceramics using aluminum hydroxide Al(OH)₃ additives. The study showed that with increasing Al(OH)₃ ratio, the flexural strength increased and the porosity decreased. Flexural strength in the range of 3–14 MPa and porosity in the range of 46–54% varied with Al(OH)₃ contents and the sintering temperature. At a sintering temperature of 1500°C, a typically porous mullite-bonded SiC ceramic of porosity 47% and 14 MPa strength at 47.3% Al(OH)₃ ratio was obtained because of the increasing densification at local regions that was attributed to the oxidation-derived SiO₂ phases and greater amount of mullite. Larger grains were also strongly attached to smaller particles and there was strong bonding between the large SiC grains (see Fig. 38). The strong porous structure between SiC and mullite would result in excellent strength for ceramics. In addition, with an increase in the Al(OH)₃ ratio, the amount of alumina

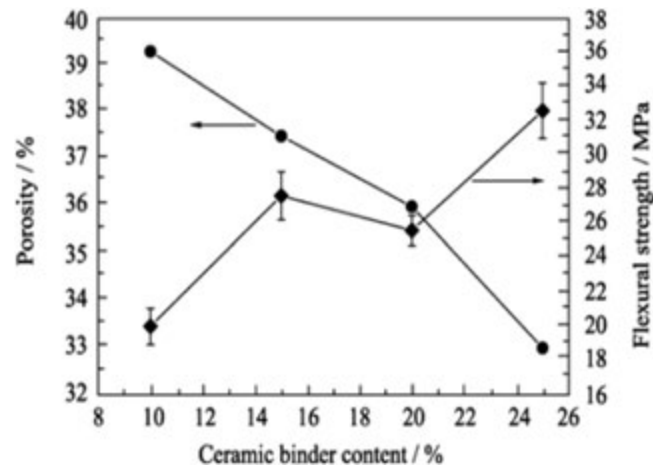


Fig. 36 Effect of ceramic binder ratio on the flexural strength and porosity of porous silicon carbide (SiC) ceramics [26].

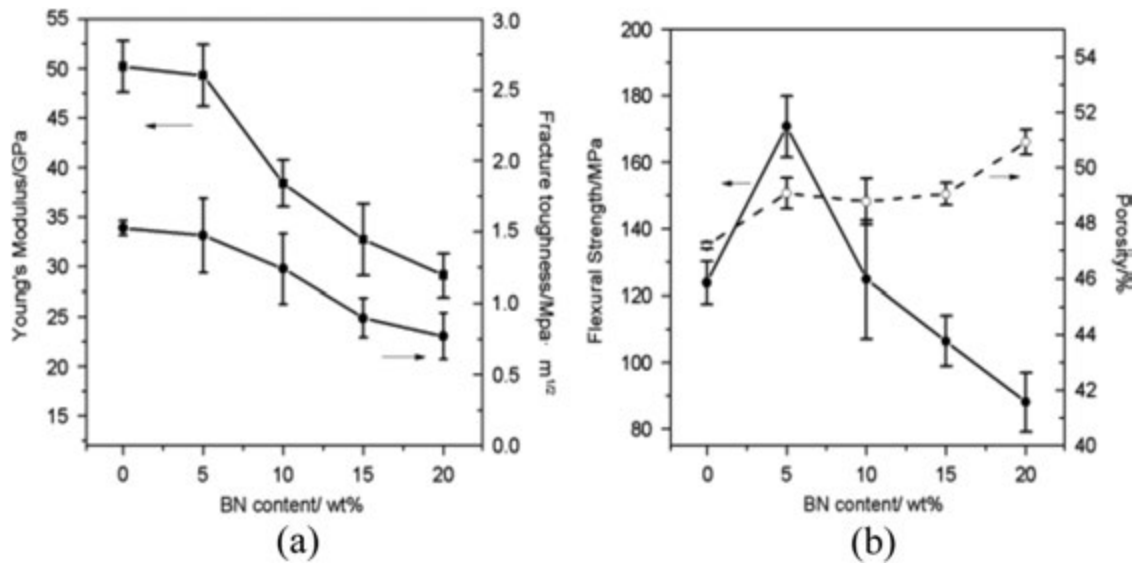


Fig. 37 (a) Fracture toughness and Young's modulus (b); the porosity and flexural strength of porous $\text{Si}_3\text{N}_4/\text{BN}$ with different ratios of boron nitride (BN) [71].

Al_2O_3 increases and with increase in $\text{Al}(\text{OH})_3$ content, the amount of Al_2O_3 increases and accelerates the reaction of mullization that leads to higher strength.

Lee *et al.* [73] studied the improvement of the compressive strength for porous mullite–alumina ceramics using coal fly ash as a source of silica (SiO_2) by the freeze-gel casting method. The study showed that with decreasing porosity, the compressive strength of porous alumina ceramics increased. After sintering at 1500°C , the compressive strength and the porosity of porous mullite–alumina ceramics were ~ 64.3 MPa and 61.2%, respectively (see Fig. 39).

It is a fact that porosity decreases with increasing sintering temperature, which results in increasing compressive strength. Also, in this case, the compressive strength of porous alumina ceramics with anisotropic pore channels will be generally lower in the perpendicular direction, compared with being parallel to the direction of freezing (see Fig. 40) [73].

Li *et al.* [74] studied the effect of chemical vapor infiltration (CVI) of Si_3N_4 on the mechanical and dielectric properties of porous Si_3N_4 ceramics prepared by a technique combining 3-D-printing and pressureless (3-D-PS) sintering. This means that, the ceramic additive was added in vapor form to improve the mechanical and dielectric properties. The study showed that the mechanical properties of porous Si_3N_4 greatly improved after the CVI process because of the increase in the ability of loading for $\beta\text{-Si}_3\text{N}_4$ particles and in the connection strength between $\beta\text{-Si}_3\text{N}_4$ particles with a decrease in porosity. The dielectric properties decrease due to the decrease in porosity. For example, the flexural strength and porosity of porous Si_3N_4 ceramics (3-D-PS) and porous Si_3N_4 ceramics (3-D-PS-CVI) were 6 MPa at 76% and 61 MPa at 64%, respectively. Eoma *et al.* [75] reported the improvement of the mechanical properties of macro-porous SiC ceramics by adding $\alpha\text{-SiC}$ with different weight ratios. The results revealed that through increasing the $\alpha\text{-SiC}$ content from 0 to 10% and from 10 to 100%, the flexural strength increases significantly

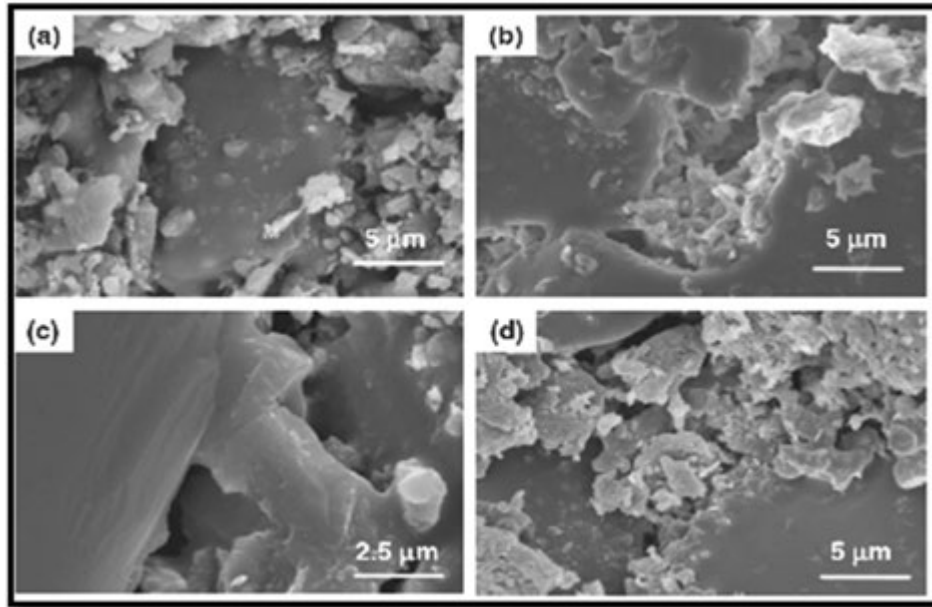


Fig. 38 Typical fracture surface of the porous mullite-bonded silicon carbide (SiC) ceramics prepared with 47.3 wt% $\text{Al}(\text{OH})_3$ and sintered for 2 h in air at (a) 1450°C, (b) and (c) at 1500°C, and (d) 1550°C [72].

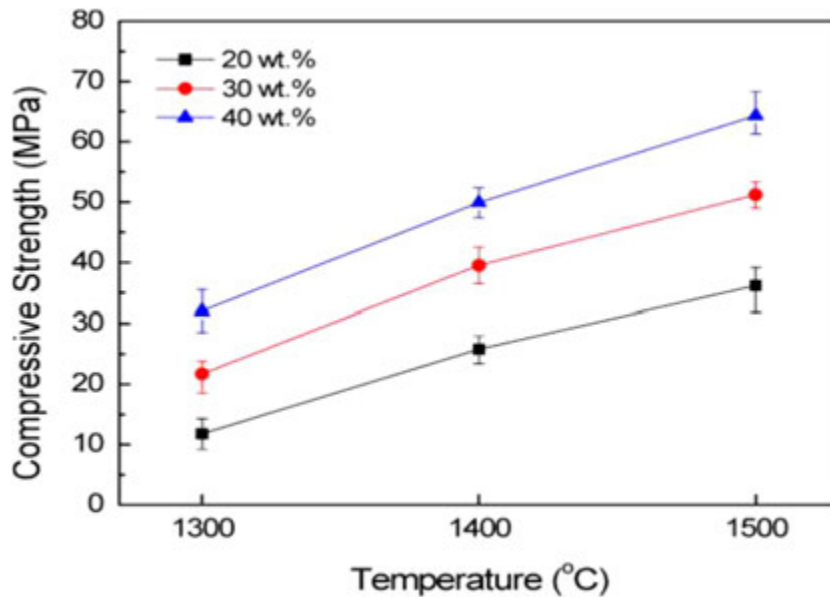


Fig. 39 Compressive strength of porous mullite composites sintered at 1300–1500°C with different solid loading [73].

from 15 to 21 MPa and from 21 to 26 MPa. The size of the pores decreased rapidly from 18 to 7 μm and then were maintained constant at 6–7 μm with increasing α -SiC content from 0 to 10% and from 10 to 100%, respectively. Thus, the increment in flexural strength with increasing α -SiC content may be attributed to a combination of the decrease in grain size from 7 to 3 μm , the decrease in the size of the pores and the decrease in the porosity from 56.4 to 55.7% (see Fig. 41).

Yu *et al.* [76] studied the effect of β - Si_3N_3 seeds (grains) addition on the mechanical properties and microstructure of porous Si_3N_4 ceramics. The study showed that with increasing the β - Si_3N_3 seed ratio from 0 to 8 wt%, the mechanical properties of porous Si_3N_4 ceramics decreased, but at 3 wt% ratio of β - Si_3N_3 seeds and porosity 42% the mechanical properties were excellent (see Fig. 42). The authors reported that the significant improvement in mechanical properties can be attributed to the porous Si_3N_4 ceramics with 3 wt% seeds having a longer pullout elongated grain length and more hexagonal holes than the porous Si_3N_4 ceramic without seeds.

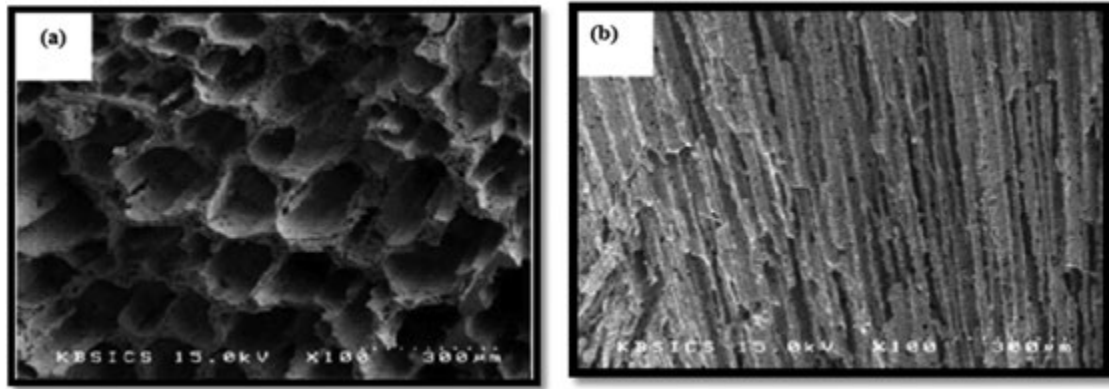


Fig. 40 Cross-section of pore channels: (a) perpendicular and (b) parallel to the freezing direction after sintering at 1400°C [73].

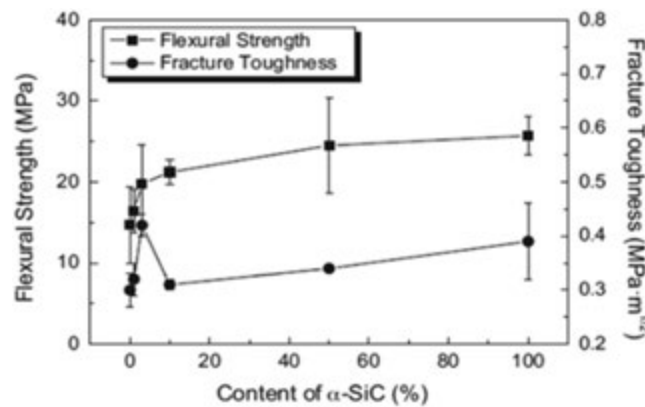


Fig. 41 Flexural strength and fracture toughness of macro-porous silicon carbide (SiC) ceramics as a function of the α -SiC content in the starting powder [75].

Xu *et al.* [77] presented the effect of SiC nano-fiber on the mechanical properties of porous alumina ceramic hollow fiber membranes by the polymer-assisted phase inversion method and the subsequent removal of the polymer and sintering at high temperatures. It is found that the bending strength of the alumina ceramic hollow fibers sintered at 1450–1510°C was enhanced by 40%, from around 154 to 218 MPa and porosity of 41.7% with 5 wt% SiC (see Fig. 43).

This excellent enhancement in the bending strength of porous ceramics may be attributed to the formation of the bridges among the alumina particles by the SiC nano-fibers, hence improving the fracture toughness of porous ceramics [77]. Hong *et al.* [78] reported the manufacturing of high porous zirconia ceramics impregnated with porous silica aerogel. The study showed that the mechanical properties of freeze cast porous zirconia ceramics enhanced upon impregnation with the silica aerogel. The compressive strength has an exponential decrease with increasing porosity. The compressive strengths of high porous zirconia ceramics were from 9.2 to 25.5 MPa at porosities from 81.5 to 68.5% before impregnation with silica aerogel and from 15.4 to 36.8 MPa at porosities between 69.3 and 46.1% after impregnation with silica aerogel, respectively. That means that the compressive strength significantly increased after impregnation with silica aerogel; this improvement is attributed to the decrease in porosity and pore size and a stiffened network due to impregnation with silica aerogel. Yan *et al.* [79] reported the effect of TiO_2 addition on the microstructure and strength of porous spinal (MgAl_2O_4) ceramics prepared from $\text{Al}(\text{OH})_3$ and magnetite. The study showed that the ratio of TiO_2 added to the porous spinal ceramics affected the neck bonds, the pore distribution, the formation of the liquid phase at the sintering temperature and changed the porosity, hence affecting the strength of the porous spinal ceramics. Therefore with increasing TiO_2 contents the average pore size, strength and liquid content at sintering temperature increased and the neck bonds developed better, while the porosity decreased with optimized porous spinal ceramics at 1.5 wt% TiO_2 ratio. This gives high flexural strength (8.5 MPa), high compressive strength (21.2 MPa), high apparent porosity (53.0%), and small average pore size (5.9 μm) (see Fig. 44).

In addition, the increase in strength may be attributed to three factors. The first important factor is the formation of a well-developed neck among the particles (see Fig. 45). The second is the porosity. The last is the particles densification that would result in higher strength. With increasing TiO_2 , the particles become denser, the porosity decreases and the neck bonds among the

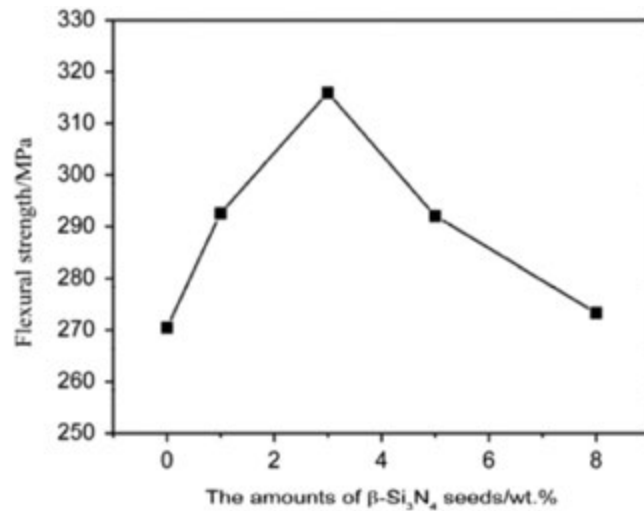


Fig. 42 Flexural strength with increasing the ratio of β -silicon nitride (Si₃N₄) seeds [76].

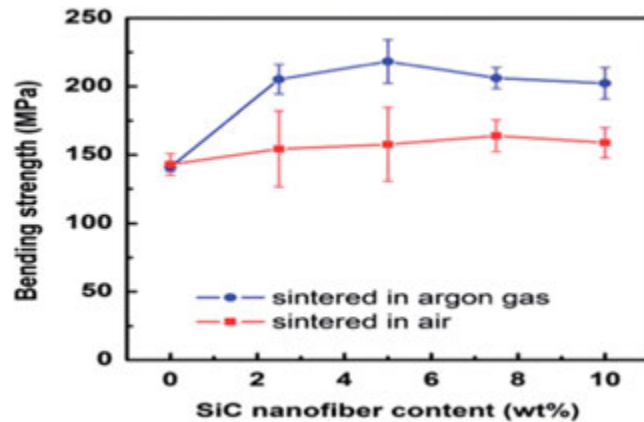


Fig. 43 Bending strength of hollow fibers with different amounts of silicon carbide (SiC) nano-fibers sintered at 1450°C in air or argon [77].

particles become coarser, which leads to an increase in strength [79]. Table 4 shows examples of the effects of ceramic additives on the mechanical properties of some porous ceramic materials.

Effects of Metal Particles Additives

The use of metal particle additives is another factor to improve the mechanical properties of porous ceramic materials. Porous ceramic materials have low mechanical properties because of the porosity. Therefore, several attempts have been made to improve the mechanical properties of porous ceramic.

Falamak *et al.* [80] reported the effect of adding aluminum particles on the mechanical properties of alumina membranes by using the reaction bonding of aluminum oxide (RBAO) process. The study showed the production of alumina membranes with greater permeability and at the same time possessing high flexural strength compared to traditional alumina membranes. The porosity and flexural strength of traditional alumina membranes and alumina membranes fabricated by RBAO were 35.73 vol%, 64.77 MPa and 32.73 vol%, 108.5 MPa, respectively, for alumina membranes ceramics sintered at 1450°C with compaction pressure of 95.5 MPa. This means that with increasing Al wt% content, the flexural strength increased and porosity decreased (see Fig. 46).

This can relate to (1) improved sintering due to the generation of very active secondary particles during the sintering step and oxidation; (2) the existence of more bonds in the initial green compact due to the higher content of ductile Al particles. Oh *et al.* [81] studied the fabrication of Al₂O₃/Cu nanocomposite using a Al₂O₃/copper oxide (CuO) and Al₂O₃/Cu nitride mixture. The study showed improvement in the fracture toughness and strength. A fracture toughness of 4.8 MPa.m^{1/2} and a strength of 953 MPa were measured for the composite, compared to a pure alumina fracture toughness of 3.6 MPa.m^{1/2} and a strength of 536

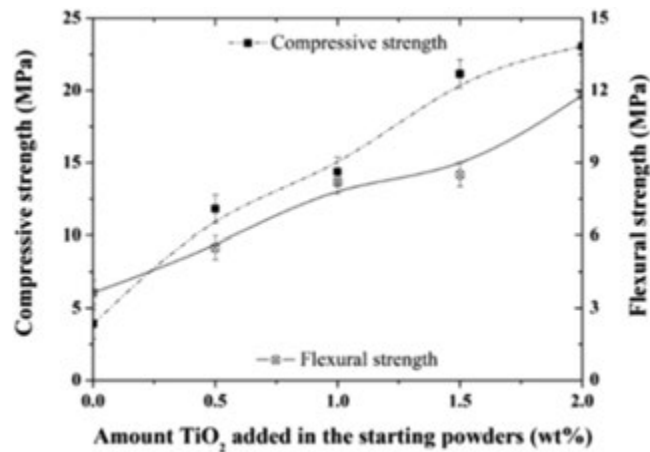


Fig. 44 Compressive and flexural strengths of sintered specimens with different ratio of TiO₂ [79].

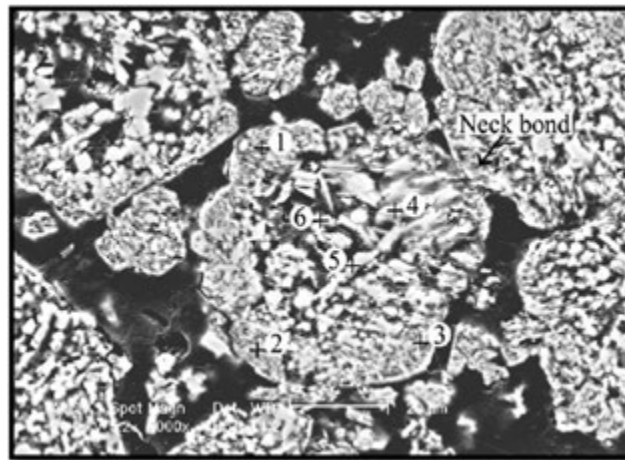


Fig. 45 Microstructure of porous spinal (MgAl₂O₄) ceramics with 1% TiO₂ [79].

MPa. The toughening and strengthening of the composites were explained by crack bridging/deflection and the refinement of the microstructure, respectively (see Fig. 47). But this ceramic is not a porous ceramic.

Clegg and Paterson [82] reported ductile particle toughening of HAP using ammonium hexachloroplatinate (ACP) as a source of platinum particles. It is found that through increasing the volume fraction of platinum particles, the fracture toughness of porous HAP ceramics doubles the value of the untouched HAP. This improvement in fracture toughness may be attributed to the crack bridging mechanism. Wang *et al.* [83] reported that reticulated porous ceramic (RPC) as Si₃N₄-Al₂O₃-SiO₂ can be fabricated using replication techniques by adding 5 wt% aluminum particles to β -Si₃N₄. The study showed that the fracture toughness and strength of RPC were improved by adding aluminum powder. This enhancement in the mechanical properties is attributed to the crack bridging mechanism (see Fig. 48).

Li *et al.* [84] studied the RBAO technique for the preparation of macro-porous alumina ceramics with high fracture toughness by the addition of aluminum (Al) powder with ratios of 4, 8, 12, 16, 20 wt%. The study showed that aluminum (Al) powder plays a significant role in the improvement of the mechanical properties of macro-porous alumina ceramics, especially in the enhancement of the bending strength and the fracture toughness. The bending strength and the fracture toughness are 137 and 2.0 MPa.m^{1/2}, respectively. These values are 2.6 and 2.0 times greater than those of porous alumina ceramics without Al additives, being 52 MPa and 1.1 MPa.m^{1/2} for the bending strength and the fracture toughness, respectively, and manufactured at the same temperature. This improvement in the mechanical properties may be attributed to the increase in densification and the decrease porosity with increased Al contents (see Fig. 49).

Manoj *et al.* [85] presented the effect of an aluminum source (Al, AlN, Al₂O₃, and Al (OH)₃) on the flexural strength of mullite-bonded porous SiC ceramics. It is found that after sintering at 1450 and 1550°C for 6 h of porous ceramic composites for different aluminum sources, porosity and specific strength range are 17%, 14–19 kN.m/kg and 42%, 5–9 kN.m/kg, for a porous ceramic with an Al₂O₃ source and a porous ceramic with an AlN source, respectively. This variation in strength is attributed to the sintering reactions and the mullitization process. Hence, for the Al₂O₃ source, mullite-silica grains were strongly adhered and connected

Table 4 Examples of ceramic additive effects on mechanical properties of some porous ceramic materials

Author	Work conditions								Major finding		
	Porous materials	Ceramic additive (%)	Method	Rang of sintering temperature (final sintering)	Rang of pressure (MPa)	Mixing method	Pore forming ratio (%) and size (μm)	Sintering time (soaking) time (h)	Pore size (μm)	Porosity ratio	Mechanical properties
Yan <i>et al.</i>	Spinel (MgAl_2O_4)	TiO_2 (0–2 wt%)	Powder metal-lurgy in situ decomposition pore forming	1600°C	100	Ball milling (3 h)	–	3 h	Small (0.1–1.5 μm) and large of (1.5–10 μm)	46–62%	The porosity and average pore size decreased. Flexural, compressive strength increased from 3.6 to 11.8 MPa, 3.9 to 23.1 MPa, respectively, with increasing TiO_2 ratio [79]
Hong <i>et al.</i>	Zirconia	Nano porous silica aerogel	Sol gel and freeze cast	1550°C	–	Mixing (10 min) and aging 24 h	–	50 min	10–30 nm	46.5–69.8%	The compressive strength increased from 9.2–25.5 to 15.4–36.8 MPa. Decreased porosity and pore size, as well as stiffened network due to impregnation with silica aerogels, contributed to the increased compressive strength of the final ceramic-aerogel systems [78]
Xu <i>et al.</i>	Alumina	Silicon carbide (SiC) nano-fiber (2.5–10.0 wt%)	Polymer-assisted phase inversion method	1450–1510°C	–	Ball milling (48 h)	–	5 h (with argon gas and without argon gas)	1.25–1.35 μm	37.5–42.8%	The bending strength of alumina ceramic hollow fibers sintered at 1450–1510°C was enhanced by 40%, from around 154 to 218 MPa when a small quantity of SiC nano-fibers 5 wt% was incorporated with argon gas [77]
Yu <i>et al.</i>	Silicon nitride (Si_3N_4)	β - Si_3N_4 (0–8 wt %)	Powder metal-lurgy (conventional sintering)	1750°C	–	Wet milled in anhydrous alcohol for 24 h	–	1.5 h Under nitrogen pressure 0.225 MPa	–	42%	With the increase of β - Si_3N_4 seeds up to 3 wt%, under a porosity of about 42%, superior mechanical properties, 315.98 MPa [76]
Eoma <i>et al.</i>	SiC	α - and/or β -SiC (0–100 wt%)	Powder metallurgy	1950°C	50	Ball milling (24 h)	–	4 h In argon	6–18 μm	58.4–54.7%	The flexural strength increased with increasing α -phase content and showed a maximum strength of 26 MPa at a porosity of 56% when the starting material contained 100% α -SiC particles The maximum toughness 0.42 MPa. $\text{m}^{1/2}$ occurred when the α -SiC content was 3 wt% because of the optimum grain size ($\sim 15 \mu\text{m}$) of the platelet α -SiC grains [75]
Li <i>et al.</i>	Si_3N_4	Vapor infiltration of Si_3N_4 (chemical vapor infiltration (CVI))	3-D-printing and pressureless (3-D-PS) sintering and CVI	1800°C	–	Ball milling (24 h)	–	0.5–2 h) Under nitrogen pressure (0.3 MPa	–	64–76%	The mechanical properties of porous Si_3N_4 greatly improved after the CVI process The flexural strength and porosity of porous Si_3N_4 ceramics (3-D-PS) and porous Si_3N_4 ceramics (3-D-PS-CVI), were 6 MPa – 76% and 61 MPa – 64%, respectively [74]

(Continued)

Table 4 Continued

Author	Work conditions								Major finding		
	Porous materials	Ceramic additive (%)	Method	Range of sintering temperature (final sintering)	Range of pressure (MPa)	Mixing method	Pore forming ratio (%) and size (μm)	Sintering time (soaking) time (h)	Pore size (μm)	Porosity ratio	Mechanical properties
Lee <i>et al.</i>	Mullitealumina	Coal fly ash as a source of silica	Freeze-gel casting	1200–1500°C	–	Ball milling (24 h in ethanol)	–	2 h	26–43 μm	84.7–61.2%	With increasing solid loading from 20 to 40 wt%, the sintered porosity 84.7–61.2% decreased in inverse proportion to the sintering temperature, while the compressive strength 11.8–64.3 MPa increased with temperature After sintering at 1500°C with 40 wt% solid loading, the mullite–alumina composite with a porosity of 61.2% exhibited a compressive strength of ~64.3 MPa [73]
Kumar <i>et al.</i>	Mullite-bonded SiC	Aluminum hydroxide $\text{Al}(\text{OH})_3$ (14.5 to 47.3 wt%)	Powder metallurgy	1450–1550°C	50	Ball milling (24 h)	–	2 h	5–40 μm	46–54%	The porosity decreased and flexural strength increased with an increase in $\text{Al}(\text{OH})_3$ content [72]
Yao <i>et al.</i>	Si_3N_4 /boron nitride (BN)	BN (0–20 wt%)	Powder metallurgy (via nitridation of silicon powder)	1680°C	10	Ball milling (24 h) in ethanol	–	2 h	–	47–51%	Both Young's modulus and fracture toughness of porous Si_3N_4 /BN ceramics decreased with increasing BN content, but the flexural strength significantly improved 170 MPa with 5% BN Low shrinkage and machinable properties with increase in the BN ratio Porosity increase with increasing BN ratio [71]
Guo <i>et al.</i>	Cordierite	La_2O_3 (0 and 5%) and rice husk as a source of silica	Powder metallurgy	1000–1350°C	20	Ball milling (1 h)	Rice husk	5 h	–	42.4–45.02%	The flexural strength improved from 2.42 MPa without using La_2O_3 to 11.38 MPa at 5 wt% of La_2O_3 , while the porosity exhibited a slightly increase in range of 42.40–45.02% [68]
Yu <i>et al.</i>	Si_3N_4	Pure β - Si_3N_4 powder (0–8 wt%)	Powder metallurgy	1750°C	–	Ball milling (24 h) in ethanol	–	2 h	–	37–42%	Porous Si_3N_4 ceramics with a porosity of 44% and the flexural strength of 330 MPa showed good mechanical properties by adding 3 mass% β - Si_3N_4 powder [2]
Li and Yin	Si_3N_4	Lu_2O_3	Powder metallurgy	1800°C	70	Ball milling (24 h)	Phenolic resin (5–10%)	for 2 h under N_2 atmosphere of 0.3 MPa	–	40–46%	Porous Si_3N_4 with secondary phase $\text{Lu}_4\text{Si}_2\text{O}_7\text{N}_2$ has a maximum flexural strength of 207 MPa [67]

Wang <i>et al.</i>	BN/Si ₃ N ₄	BN (0–15 vol%)	Gel casting	1750°C	–	Ball milling (24 h)	–	1 h Under 0.1 MPa N ₂ atmosphere	–	48.1–53.3%	With BN contents increasing, the mechanical properties of the porous BN/Si ₃ N ₄ composite ceramics partially declined Without BN addition, the porosity, flexural strength, were 48.1%, 128 MPa, while for the 10 vol% BN/Si ₃ N ₄ porous composite ceramics, they were 49.4%, 106.6 MPa, respectively. Some improvement in machinability [65]
Li <i>et al.</i>	Si ₃ N ₄	Hexagonal BN on (25–45 vol%)	Powder metallurgy (pressureless sintering process)	1800°C	–	Ball milling (12 h) anhydrous alcohol	–	For 2 h in N ₂ gas	–	17.8–30.4%	The growth of the elongated β -Si ₃ N ₄ were hindered by h-BN additive, which resulted in the decrease of the fracture toughness of Si ₃ N ₄ /BN ceramics with increasing h-BN content from 3.4 to 1.9 MPa.m ^{1/2} and decreased flexural strength from 210 to 105 MPa [64]
Chae and Kim	SiC	Submicron SiC powder as an inert filler	Powder metallurgy	1750–1950°C	28	Ball milling (24 h) in ethanol	Poly methyl-methacrylate (PMMA) microbeads	1 h	–	49–64% with filler	The addition of SiC fillers leads to finer microstructure when sintered at 1900 and 1950°C Resulting in higher strength at an equivalent porosity than the specimens without fillers. Then dimensional control [61]
Eom and Kim	SiC	Sintering additives (Al ₂ O ₃ , Y ₂ O ₃ , MgO, SiO ₂ , and Alan)	Powder metallurgy (carbothermal reduction)	1750°C	28	Ball milling (3 h)	Hollow poly (methyl methacrylate) spheres 15–25 μ m (5%)	1 h	–	56–72%	Sintering additive composition is an efficient way to improve the mechanical strength of porous SiC ceramics [60]
Lee <i>et al.</i>	1-SiC	1-Clay, alumina, mullite and calcium carbonate (CaCO ₃)	Extrusion	1-1400°C	1-CIP (20–40)	Kneaded for 1 h in a sigma-blade mixer with additions of water	Organic additive (polymer)	1–3 h	47 μ m in the support and 10 μ m in the coating layer	1-30–40%	The CaCO ₃ additive was effective in improving the strength of the SiC hot gas filter. The SiC filter bonded with Al ₂ O ₃ additive exhibited superior hot corrosion resistance in the simulated PFBC gas environments
	2-Nickel oxide (NiO) and YSZ	2-CaCO ₃ , Y ₂ O ₃ , and ZrO ₂		2-1300–1500°C	2-400 kgf/cm ²					2-28.4–46%	Y ₂ O ₃ additives were effective to enhance the strength of NiO-ZrO ₂ anode for solid oxide fuel cell (SOFC) [57]
Guanghai Li	Alumina	Al ₂ O ₃ nanoparticle (27 nm)	Powder metallurgy	1510°C	100 and CIP 300	Ball milling (24 h) in ethanol	–	3 h	–	–	Nano-Al ₂ O ₃ addition can increase the strength, the fracture toughness and thermal shock resistance of the porous Al ₂ O ₃ ceramics [56]

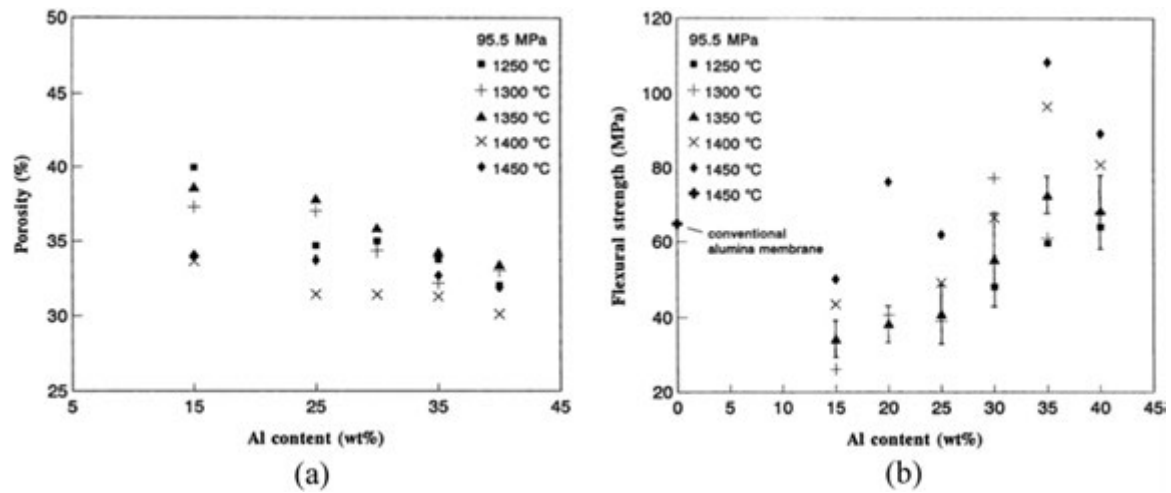


Fig. 46 Relationship between (a) porosity and (b) flexural strength with Al content in the initial powder for a compaction pressure of 191.0 MPa with different sintering temperatures [80].

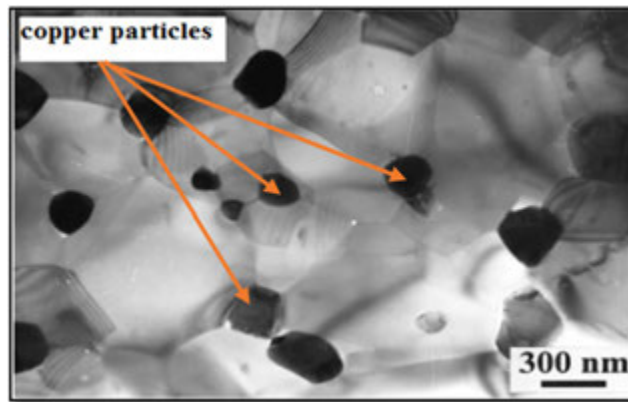


Fig. 47 Typical microstructure of the $\text{Al}_2\text{O}_3/5 \text{ vol}\% \text{ Cu}$ composites; source materials of Cu is copper oxide (CuO). Sintering conditions of composites is 1450°C and 30 MPa for 1 h [81].

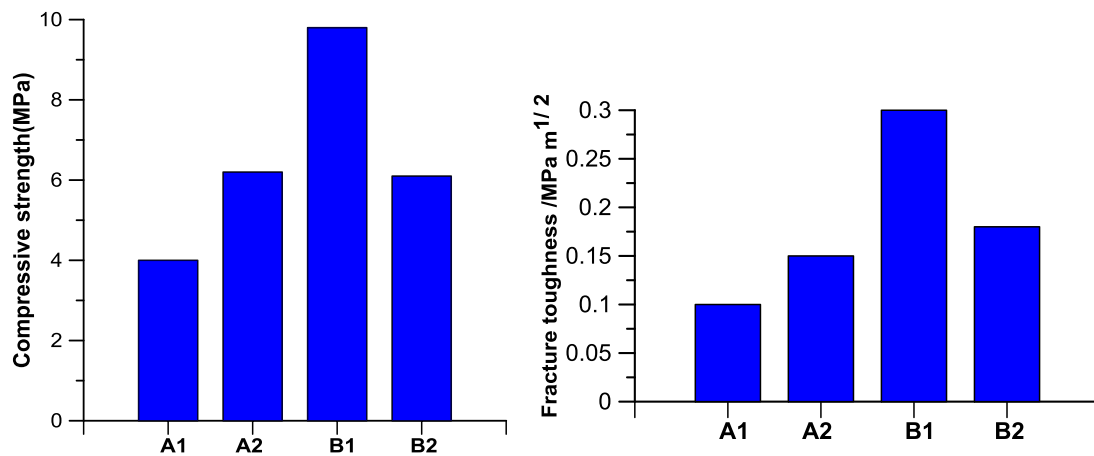


Fig. 48 Compressive strength and fracture toughness of porous ceramics A1(0 wt% Al), A2(5 wt% Al), B1(5 wt% Al), and B2(10 wt% Al) [83].

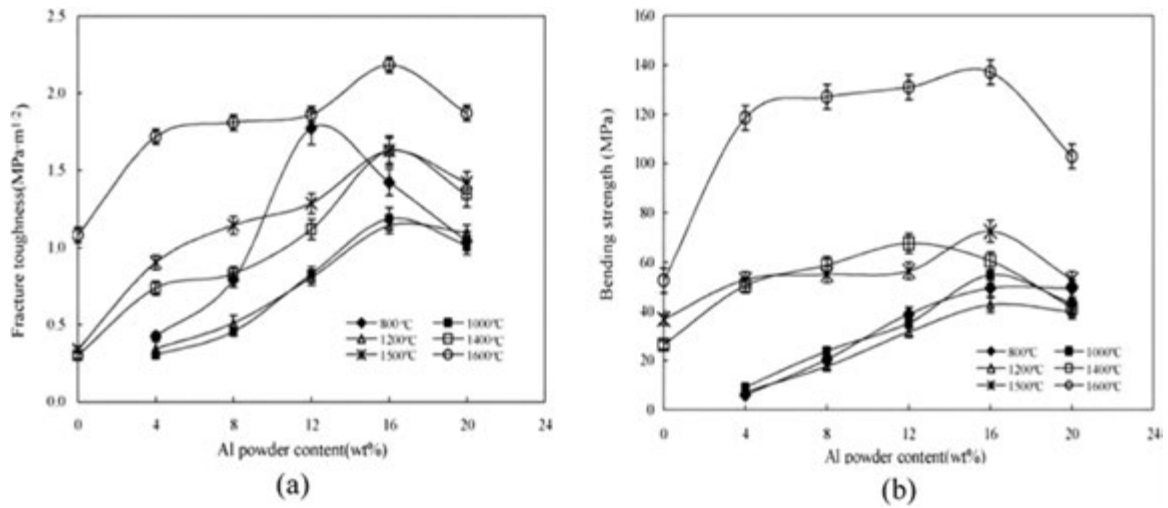


Fig. 49 Relationship between (a) fracture toughness, (b) bending strength and Al content of porous ceramics sintered at different temperatures [84].

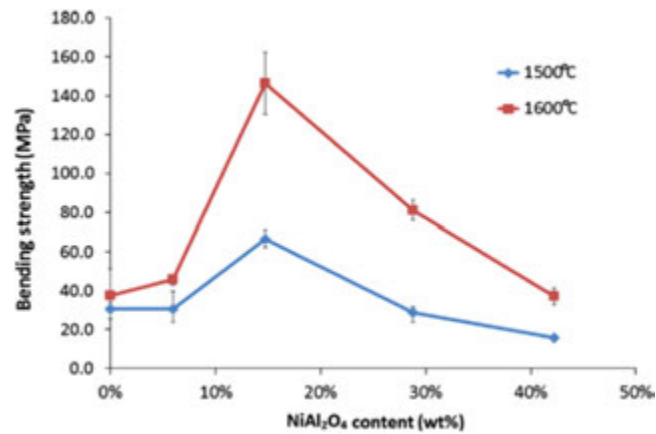


Fig. 50 Bending strength of ceramics with various NiAl₂O₄ contents sintered at 1500 and 1600°C [86].

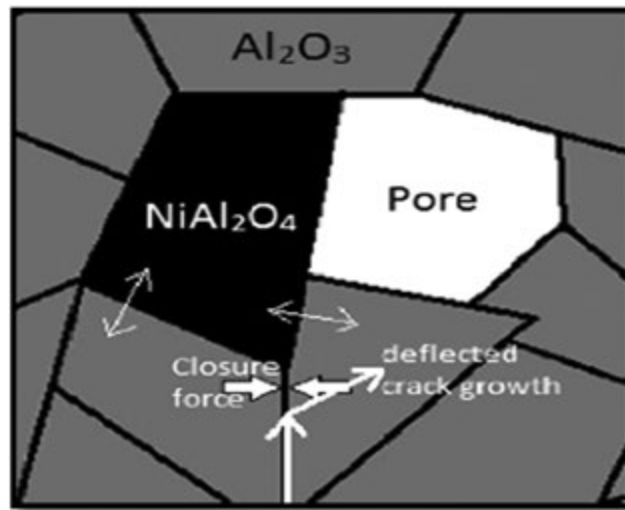


Fig. 51 Schematic diagram of grain boundary closure and stress formed by the presence NiAl₂O₄ [86].

Table 5 Examples of metal additive effects on the mechanical properties of some porous ceramic materials

Author	Work conditions								Major finding		
	Porous materials	Metal additive (%)	Method	Rang of sintering temperature (final sintering)	Rang of pressure (MPa)	Mixing method	Pore forming ratio (%) and size (μm)	Sintering time (soaking) time (h)	Pore size (μm)	Porosity ratio	Mechanical properties
Fung and Wang	Alumina	Nickel (II) oxide from nickel carbonate (0–19.1 wt%)	Powder metallurgy	1500 and 1600°C	–	Ball milling (48 h at 30 rpm)	–	5 h	–	Above 30%	The highest bending strength of 146 MPa was achieved in the porous alumina with 14.7 wt % nickel aluminate spinel phase (NiAl_2O_4) and a porosity of 30.5% The effect of sintering temperature on pore size distribution decreased with increased amount of NiAl_2O_4 [86]
Kumar <i>et al.</i>	Mullite-bonded silicon carbide	Aluminum source (Al, AlN, Al_2O_3 , and $\text{Al}(\text{OH})_3$)	Powder metallurgy	1450 and 1500°C	50	Ball milling (24 h)	–	1, 2, 6 h	–	17–42%	The porosity decreased and strength increased with sintering temperature and time The ceramics with Al_2O_3 exhibit highest specific strength, 14–19 kN.m/kg while the ceramics with AlN exhibit lowest specific strength 5–9 kN.m/kg [85]
Li <i>et al.</i>	Alumina	Al (4, 8, 12, 16, 20 wt%)	Powder metallurgy (reaction bonding of aluminum oxide (RBAO))	800–1600°C	8	Ball milling (24 h)	–	2 h	1.87	30	Al powder plays an important role in the increments of the mechanical properties of the supports, especially in the improvement of fracture toughness from 1.1 to 2 $\text{MPa.m}^{1/2}$ and bending strength from 52 to 137 MPa [84]
Wang <i>et al.</i>	Multiphase reticulated porous ceramics (RPC)	Al (5–10 wt%)	Replication	1400°C	–	Ball milling (4 h)	Polyurethane sponges	1 h	–	–	The compressive strength and fracture toughness improved owing to the crack bridging behavior Si_3N_4 RPC with additives of 5% Al and 5% Al_2O_3 yielded a compressive strength of 9.8 MPa and fracture toughness of 0.3 $\text{MPa.m}^{1/2}$ [83]
Chae <i>et al.</i>	Hydroxyapatite	Ammonium hexachloroplatinate (ACP) as a source of platinum particles (0–5 vol %)	Powder metallurgy	1250–1350°C	80	–	–	4 h	–	–	The increase in fracture toughness correlated with the volume fraction of platinum [43]
Falamaki <i>et al.</i>	Alumina	Al (15, 20, 25, 30, 35, and 40 wt%)	Powder metallurgy (RBAO)	1250–1450°C	95.5–191	Ball milling (planetary) (1 h) in acetone	–	2.5 h	Large hollow channels (10–200 mm)	25–40%	With increasing Al content, the flexural strength of porous alumina ceramics increases and the porosity decreases also can produce alumina membranes with higher permeability compared to conventional alumina membranes and, at the same time, possessing high flexural strength [80]

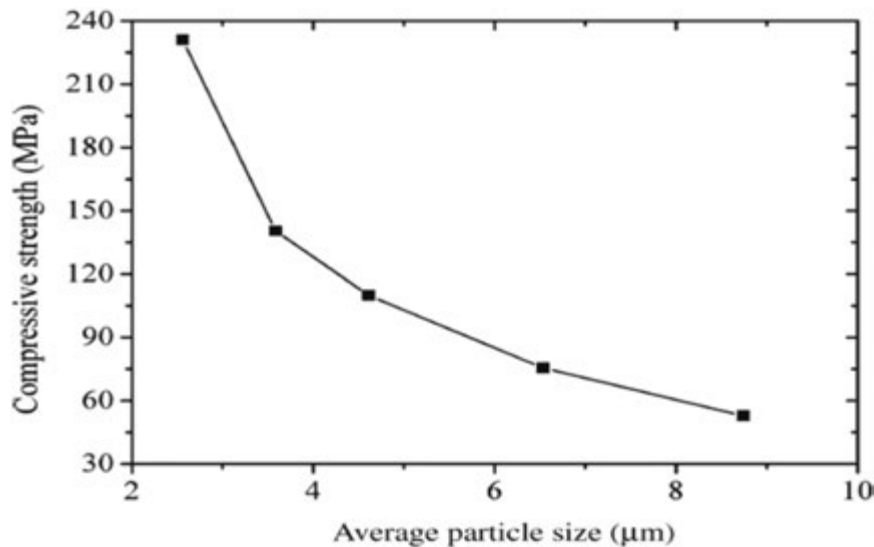


Fig. 52 Compressive strength against particle size for porous spinal ceramics sintered at 1340°C [88].

with the large SiC grains compared with the AlN source. The mullite–silica grains had poor adhesion and weak bonding, therefore the strength of the porous ceramics with the Al_2O_3 source is higher than for the porous ceramics with an AlN source. Fung *et al.* [86] studied the reinforcement of porous alumina ceramics by the nickel aluminate spinal phase in an alumina matrix via the reaction between NiO and alumina. The study showed that with a 4.7 wt% NiAl_2O_4 ratio, the porosity was 30.5% and the highest bending strength was 146 MPa in porous alumina ceramics (see Fig. 50).

They reported that the improvement in the bending strength referred to the formation of the NiAl_2O_4 phase, which would create a stress field in the matrix. This is due to thermal expansions, and thus different rates of shrinkage between the NiAl_2O_4 phase and the alumina during the sintering and cooling processes building up stress in the porous alumina. The NiAl_2O_4 phase contracted more than alumina when cooling down and generated compressive tangential stress, thus causing a closure force along the grain boundaries. This closure slowed down the growth of cracks leading to an improvement in strength for porous alumina ceramics (see Fig. 51) [86]. Table 5 shows examples of metal additive effects on the mechanical properties of some porous ceramic materials.

Effects of Particle Size

Kennedy *et al.* [87] reported the effect of SiC particle size on the flexural strength of porous self-bonded SiC ceramics. The study showed that incorporating 0.7 μm SiC particles into the ceramic material containing 25 μm SiC particles increased the flexural strength by three times, from 11.7 MPa up to 35.5 MPa after sintering at 1800°C, and the porosity decreased from 47 to 46%. This improvement in the flexural strength could be attributed to enhanced necking and reduced porosity with increased sintering temperature. Yan *et al.* [88] studied the effect of particle size on the strength and microstructure of porous spinel ceramics prepared by the pore forming in situ technique. It was found that the particle size strongly affects the microstructure and strength. With decreasing particle size, the apparent porosity decreases gradually; there was good neck development among the particles and an acceptable pore distribution leading to an increase in the compressive strength (see Fig. 52).

Li *et al.* [89] studied the effect of the SiC particle size, the molding pressures and the bonding phase contents on the flexural strength of porous SiC ceramics used as hot gas filters. It is found that SiC the particle size, the molding pressure and the bonding phase contents affected the fracture point area of the SiC particles in the fracture surface, hence affecting the flexural strength of the porous SiC ceramics. Yan *et al.* [90] studied the effect of particle size on the pore characterization and strength of porous cordierite–mullite ceramics manufactured by pore forming in situ. The results revealed that the particle size strongly affects the formation of cordierite and mullite, and changes the pore characterization and strength. The strength increases with decreasing particle size and the increase in sintering temperature because of the porosity decrease, well distributed pores and good neck development. Table 6 shows examples of particle size effects on the mechanical properties of some porous ceramic materials.

Effects of Others Factors

In addition, there are other factors that have an effect on the mechanical properties of porous ceramics. Trecant *et al.* [91] studied the influence of postimplantation physico-chemical changes in macro-porous biphasic calcium phosphate (MBCP) ceramics and

Table 6 Examples of particle size effects on the mechanical properties of some porous ceramic materials

Author	Work conditions								Major finding		
	Porous materials	Particle size (μm)	Method	Rang of sintering temperature (final sintering)	Rang of pressure (MPa)	Mixing method	Pore forming ratio (%) and size (μm)	Sintering time (soaking) time (h)	Pore size (μm)	Porosity ratio	Mechanical properties
Yan <i>et al.</i>	Cordierite–mullite	17.6, 10.2, and 8.5 μm	Powder metallurgy	1370–1430°C	50	Ball milling (1, 4, and 7 h)	–	3 h	Median (11.9–5.8)	30–47%	Particle size strongly affects the formation of cordierite and mullite, and then changes the pore characterization and strength With the decrease in particle size, the sintering temperature at which the formation of cordierite and mullite takes place decreases. The pore size distribution changes from bi-peak mode to mono-peak mode, the porosity and the median pore size decrease but the strength increases [90]
Li <i>et al.</i>	silicon carbide (SiC)	87, 123, 239, and 300 μm	Powder metallurgy	1300°C	6–91	Ball milling (36 h)	Graphite (6%)	3 h	–	35.5–42.4%	The SiC-based porous ceramic composed of small SiC particles has a bigger fraction of SiC particle fracture point area in the minimum solid area of the fracture surface composed of big SiC particles. The SiC particle size has more significant effects on the flexural strength than the porosity [89]
Yan <i>et al.</i>	Spinel ceramics	8.74, 6.53, 4.61, 3.58, and 2.56 μm	Powder metallurgy (pore forming in situ technique)	1340°C	100	Ball milling (3, 6, 9, 12, and 15 h)	–	3 h	1.32–4.38	30–40%	Particle size strongly affects the microstructure and strength With decreasing particle size, pore size distribution takes place from multi-peak mode to bi-peak mode, and lastly to mono-peak mode; the porosity decreases but the strength increases [88]
Kennedy <i>et al.</i>	SiC (SBSC)	0.7, 25, 50, 65 μm	–	1700–1800°C	35 and 200 ICP	Ball milling (24 h) in ethanol	Microbeads ($\sim 20 \mu\text{m}$)	2 h	50	45–52%	Incorporating 0.7 μm SiC particles into ceramic material containing 25 μm SiC particles increased the flexural strength by three times, from 11.7 MPa up to 35.5 MPa after sintering at 1800°C [87]

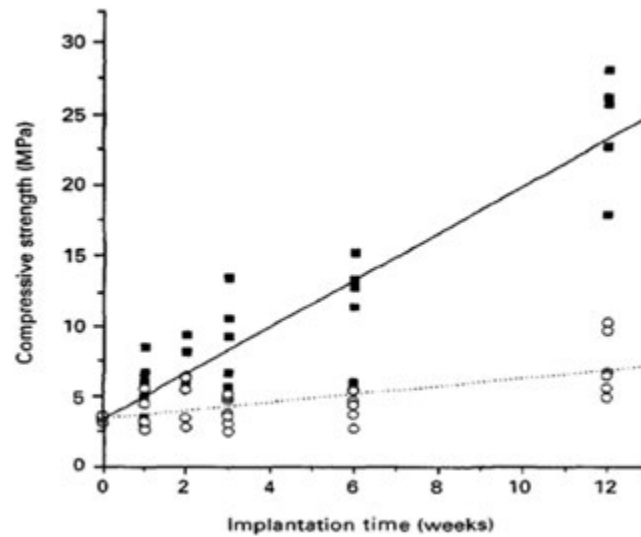


Fig. 53 Compressive strength of macro-porous biphasic calcium phosphate (MBCP) as a function of implantation time [91].

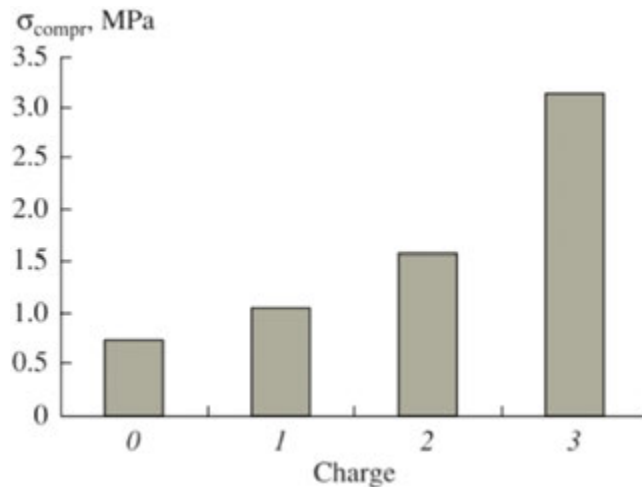


Fig. 54 Effect of the conditions of activation of the cordierite charge on the compressive strength of high porosity ceramics [44].

the impact on its mechanical strength. It is found that the mechanical properties of MBCP ceramics increase with increasing implantation times due to the decrease in microporosity and the precipitation of needle-like crystals. This means that a physico-chemical process could improve the mechanical properties of MBCP ceramics (see Fig. 53).

Zhu *et al.* [92] reported the effect of vacuum degassing on the strength of SiC RPCs manufactured by the polymeric sponge process. The study showed that vacuum degassing has a significant influence on the mechanical properties of porous SiC ceramics. After degassing, the flexural strength increases from 2.34 to 3.18 MPa. They reported that the enhancement in the strength of porous alumina ceramics following the degassing process was attributed to the increase in the relative density from 0.21 to 0.22 and the large defects in the struts. Kawai *et al.* [93] studied the effect of grain size distribution on the strength of porous Si₃N₄ ceramics composed of elongated β-Si₃N₄ grains. It is found that the strength of the porous Si₃N₄ ceramics does not always increase with the decreasing porosity but depends on the grain length of β-Si₃N₄; a longer grain leads to a higher strength. Komlev *et al.* [94] presented the strength enhancement of porous HAP ceramics following polymer impregnation. The study showed that porous HA infiltrated with 4% PVA and 10% gelatin solutions exhibited a minimum tensile strength of 5.7 and 9.8 MPa, respectively; these values were reached under a vacuum of 1.33 Pa for 30 min. It is noticeable that the HAP/gelatin composites have higher tensile strengths than those with PVA. Increasing the PVA concentration up to 10% does not result in the enhancement of the strength of porous ceramics. The effect depends on the properties of the microstructure of the matrix, the polymer and the conditions of the impregnation experiment. Antsiferov and Porozova [44] studied the effects of the mechano-chemical activation of the cordierite charge on the strength of porous cordierite using polymeric-matrix duplication. Before mixing the raw material in to a charge, these raw materials were subjected to wet grinding and drying. The charge activation and mixing were conducted in the drying mode

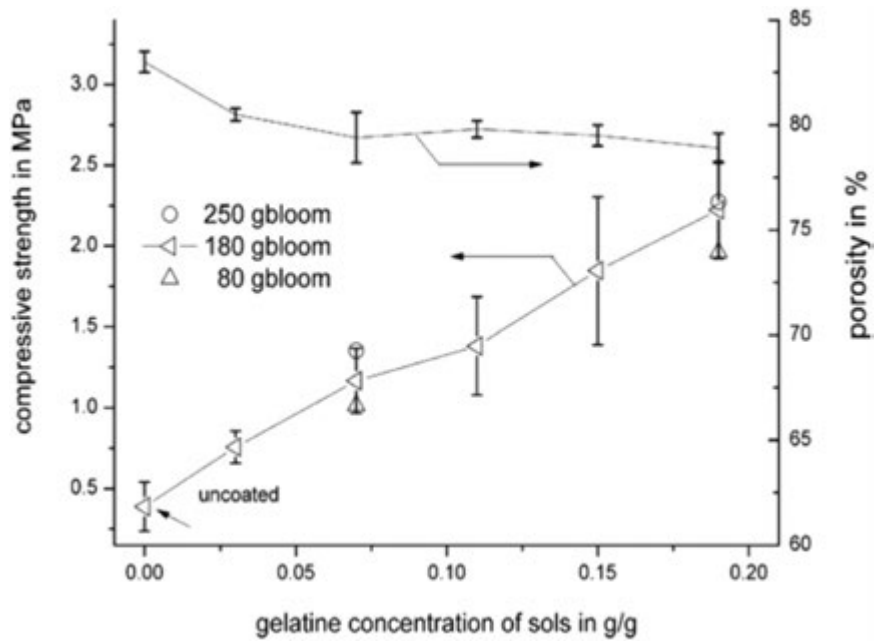


Fig. 55 Compressive strength of gelatin coated $T_{(sol)}=50^{\circ}\text{C}$ porous hydroxyapatite (HAP)-ceramics as a function of gelatin concentration in the sols and the type of gelatin [96].

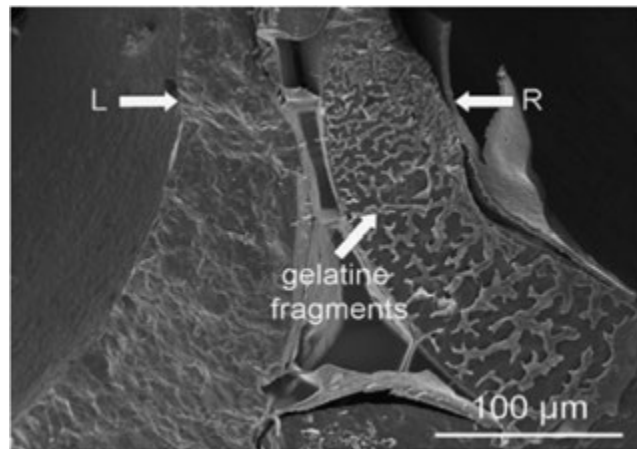


Fig. 56 Transversal crack sealing with applied gelatin coating. Scanning electron microscope (SEM) micrograph of gelatin fragments on the fracture surface of a transversal crack for hydroxyapatite (HAP)-ceramics which have been coated with highly concentrated gelatin sol of 0.19 g/g [96].

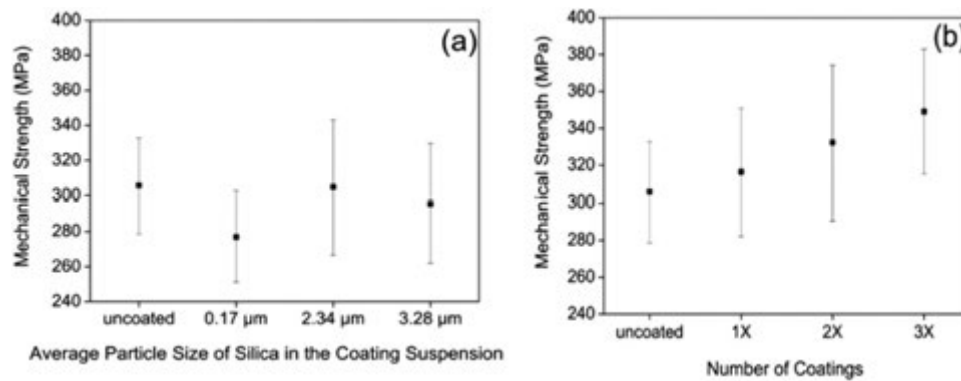


Fig. 57 Mechanical strength (a) porous alumina ceramics coated with SiO_2 suspension and (b) coated with polysiloxane [97].

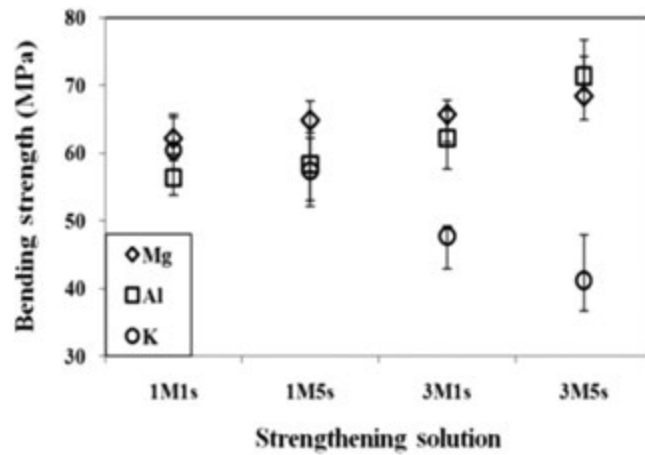


Fig. 58 Changes in the bending strength of porous ceramics by concentration and infiltration time of the strengthening solutions [98].

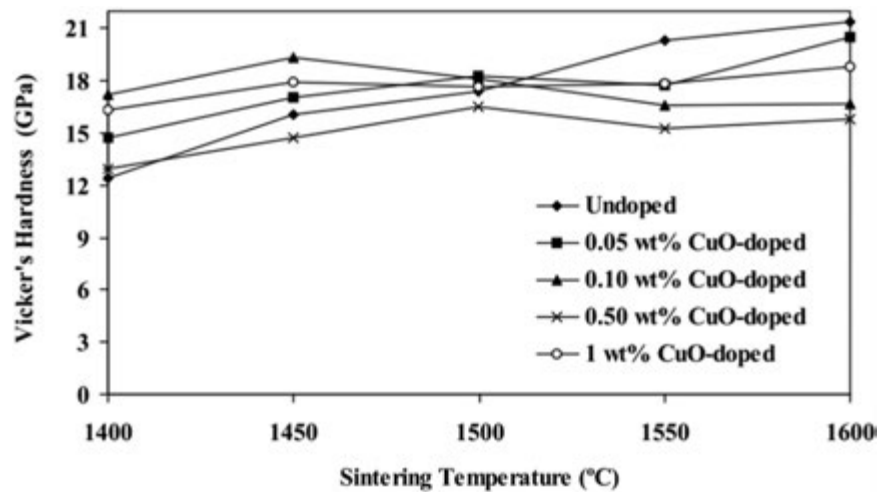


Fig. 59 Effect of copper oxide (CuO) doping on the hardness of alumina ceramics [99].

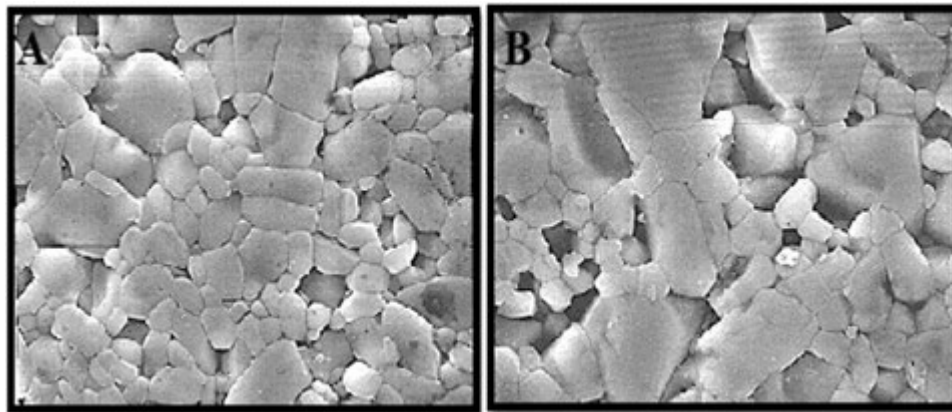


Fig. 60 (A) Undoped Al_2O_3 and (B) 1 wt% copper oxide (CuO)-doped, Al_2O_3 . Microstructure of alumina sintered at 1600°C. Note that abnormal grain growth occurred in the CuO-doped alumina [99].

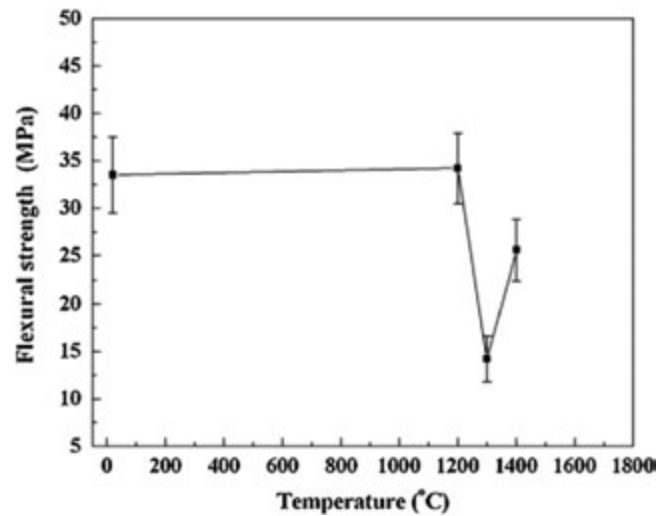


Fig. 61 Effect of pre-oxidation on the strength of porous silicon nitride (Si_3N_4) ceramics [99].

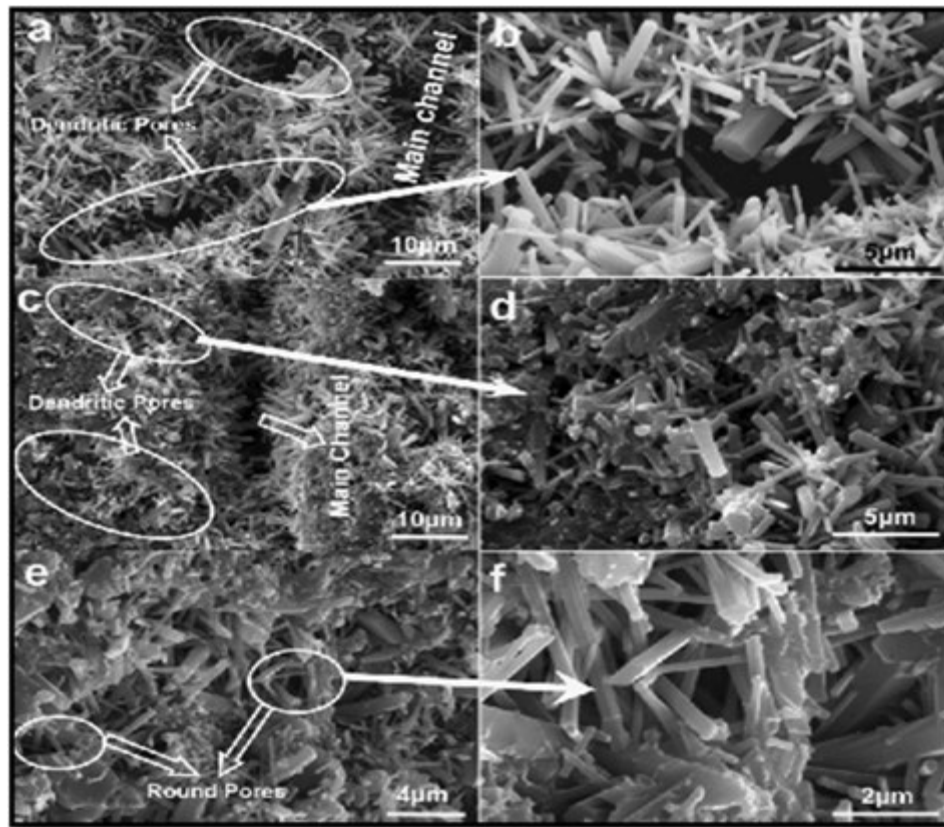


Fig. 62 Pore microstructure of porous silicon nitride (Si_3N_4) ceramics with different solid contents indicating that the increased solid content strongly affects the structure of the pores with a great number of fibrous Si_3N_4 grains protruding from the internal walls of the pores: (a), (b) 30 vol%; (c), (d) 40 vol%; and (e), (f) 50 vol% [100].

with the introduction of titanium oxide or carbide in an aqueous medium with the addition of Trilon B (a disodium salt of ethylenediaminetetra acetic acid (EDTA) known as an active complexon). This process is known as mechano-chemical activation. The study showed that charge activation by the addition of Trilon B in an aqueous medium is possible, leading to attainment a steady increase in strength with a satisfactory quality of the cordierite obtained. The addition of titanium carbide intensified the

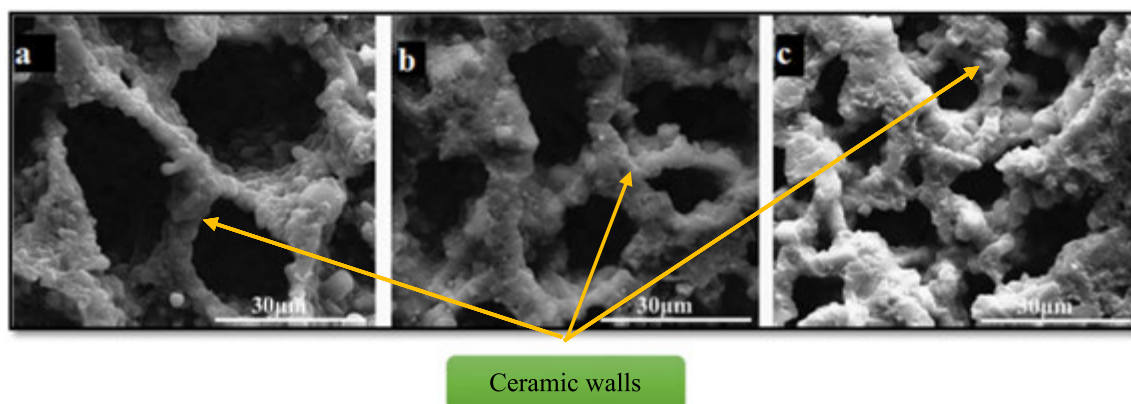


Fig. 63 Scanning electron microscope (SEM) micrographs of the porous Y- α -SiAlON ceramics sintered at 1900°C for 1 h with different solid loading contents of (a) 10 vol%, (b) 20 vol%, and (c) 30 vol% [101].

process of cordierite synthesis and ensured a considerable growth in strength for highly porous permeable cordierite ceramics. They reported that this improvement in strength was attributed to a glassy phase in the materials as shown in Fig. 54 [44].

Yao *et al.* [95] studied the effects of the fabrication parameters on the mechanical properties of sintered reaction bonded porous Si_3N_4 ceramics. The studies showed that with decreasing Si particle size, the shrinkage increases, the microstructure becomes finer and the porosity increases from 42.14 to 46.54% leading to an improvement in the flexural strength from 141 to 165 MPa. Normally, with increasing porosity, the flexural strength decreases, but in consideration of the difference in microstructure, the high respect ratio and the fine microstructure, this results in increasing the interlocking grains and improving the flexural strength. Using nano- Y_2O_3 as a sintering additive leads to the generation of fine α - Si_3N_4 grains. However, the high content of α - Si_3N_4 > 20% after nitridation also works as a nuclei site for precipitation and consumes a large amount of the Si-N liquid phase, which would result in minimizing the improvement of flexural strength because of the restrained growth of fine α - Si_3N_4 grains. Another factor which affects the mechanical properties of porous ceramics is a gelatin coating. Dresslern *et al.* [96] reported the effect of a gelatin coating on the compressive strength of porous HAP ceramics. The study showed that a gelatin coating increases the toughness of porous coated ceramics. They reported that this increase in toughness is attributed to the bridging of the crack, which is facilitated by the applied gelatin coating. The ceramics coated with higher concentration gelatin sols (0.19 g/g) would result in higher compressive strength of 2.22 MPa compare to uncoated porous ceramics with a compressive strength of 0.38 MPa as shown in Fig. 55.

In addition, with increasing gelatin concentration, the porosity decreases slightly. This effect is due to the increased amount of remaining gelatin material within the transversal cracks after drying (see Fig. 56). Applying different gel strengths at different temperatures has a slight effect on the compressive strength of the coated ceramics [96].

Takaaki and Todo [53] studied the effect of collagen coating on the compressive strength of porous bioceramic bone substitute (beta-tricalcium phosphate (β -TCP)). It is found that the modulus and compressive strength of porous (β -TCP) ceramics significantly improve with collagen coating. Junkes *et al.* [97] presented the influence of the coatings on microstructure and mechanical properties of pre-ceramic paper-derived porous alumina substrates. The study showed that the polysiloxane polymer infiltration into the paper-derived alumina substrates is more effective in closing the porosity of the surface compared with the silica suspension. Coating with polysiloxane gives a mechanical strength reaching ~ 350 MPa, while with the silica suspension it has a mechanical strength close to ~ 300 MPa. Polysiloxane is more effective at pore filling, resulting in a decrease of the open porosity; hence a higher mechanical strength has been achieved. Meanwhile, the silica suspension presents a higher viscosity, which only infiltrates the pores at the alumina's surface so that the mechanical strength is relatively low (see Fig. 57).

Kim *et al.* [98] used the surface infiltration of the strengthening materials to improve the strength of porous ceramics. The solutions aluminum nitrate hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), MgCl_2 , and KNO_3 have been used as surface strengthening materials to improve the strength of light weight pottery (porcelain slurry) using the slip casting method. The study showed that the bending strength of porous ceramics soaked in an Mg solution increased with increasing infiltration time and concentration, while the bending strength increased to as much as 26% greater than the porous ceramics which were not soaked in the strengthening solution. Because the magnesium led to the formation of cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) and cordierite has a low thermal expansion coefficient ($2-3 \times 10^{-6}/\text{K}$), which is lower than of the other material's thermal expansion coefficient ($6-7 \times 10^{-6}/\text{K}$), this results in generating a residual stress hence increasing the bending strength. Meanwhile, porous ceramics soaked in a potassium solution present a lower strength than ordinary porous ceramics. In addition, porous ceramics that have been soaked in 3 M Al solution for 5 s showed 30% higher levels of bending strength compared to ordinary light weight porous ceramics. The increase in the bending strength can be attributed to the formation of the mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) phase because the main component in the pottery's raw materials and the solutions were SiO_2 and Al_2O_3 , respectively (see Fig. 58).

Some researchers also studied the oxidation degree for ceramic powders during sintering and its impact on the mechanical properties of porous ceramics. Ramesh *et al.* [99] presented the effects of adding small amounts of CuO on the sintering and the mechanical properties of alumina ceramics. Small additions of CuO up to 1 wt% can be beneficial to the sintering of 99.8% pure alumina ceramics. All CuO-doped Al_2O_3 could be sintered at a low temperature (e.g., 1400°C) to attain above 94% theoretical

Table 7 Examples of other factors affecting the mechanical properties of some porous ceramic materials

Author	Work conditions								Major finding		
	Porous materials	Others factors	Method	Rang of sintering temperature (final sintering)	Rang of pressure (MPa)	Mixing method	Pore forming ratio (%) and size (μm)	Sintering time (soaking) time (h)	Pore size (μm)	Porosity ratio	Mechanical properties
Eoma <i>et al.</i>	Silicon carbide (SiC)	Forming method (compression molding, injection molding, and extrusion)	Compression molding, injection molding, and extrusion	1750°C	For compression molding (28) and injection molding, and extrusion (1)	Ball milling	–	For 1 h in argon	–	72.4–84%	The compression molding process leads to more homogeneous microstructure than the other forming methods, resulting in a superior compressive strength of 20.6 MPa at 72.4% porosity; extrusion-molding leads to a higher porosity (84%) than the other forming methods (72–74%) because of the higher expansion of the expandable microspheres; and the injection molding process leads to partial segregation of the expanded microspheres and results in the formation of large pores [18]
Hou <i>et al.</i>	α -SiAlON	Solid loading (10–20–30 vol%)	Freeze casting	1900°C	–	Ball milling (24 h)	Polyurethane sponge	For 1 h under a nitrogen gas pressure of 0.6 MPa	8–19 μm	23.1–64.3%	With the increase in initial solid loading content from 10 to 30 vol%, the porosity decreased from 64.3 to 23.1% and the average pore size decreased from 19 to 8 μm . As a result, the flexural strength increased significantly from 72.4 to 190.2 MPa; the fracture toughness increased from 1.20 to 3.48 $\text{MPa}\cdot\text{m}^{1/2}$ [101]
Veljovic <i>et al.</i>	Silicon nitride (Si_3N_4)	Solid content (30, 40, 50 vol%)	Freeze casting	1800°C	–	Ball milling (20 h)	–	1.5 h Under a 0.1 MPa nitrogen atmosphere	–	40.2–64.1%	The pore structure, porosity, α → β - Si_3N_4 transformation and mechanical properties of porous silicon nitride ceramics were strongly affected by the solid contents of the slurries. The flexural strength and the fracture toughness increase with increasing solid contents from 57 to 189 MPa and 1.1 to 3.5 $\text{MPa}\cdot\text{m}^{1/2}$, respectively. The pore structure changes from aligned channels with dendrites into round pores with decreasing pore size [48]
Zhang <i>et al.</i>	Si_3N_4	Pre-oxidation	Freeze casting	1800°C	–	Ball milling (12 h)	–	1 h Under 0.05 nitrogen	–	62%	As the pre-oxidation temperature increased from 1200 to 1400°C, firstly, the flexural strength of the pre-oxidized ceramics remained almost constant at 1200°C, and then decreased to 14.2 MPa at 1300°C, but finally increased to 25.6 MPa [6]

Zeng <i>et al.</i>	Mullitized porous oxidation-bonded SiC (OBSC)	Preheat-treated aluminosilicate (PHAS)	Powder metallurgy (in situ reaction bonding)	1350–1550°C	56 MPa	Ball milling (24) in ethanol	Graphite (10 μm)	2 h	2.8–4 μm	With PHAS (35%) Without PHAS (51.1%)	Porous SiC ceramics with 5.0 wt% PHAS addition exhibited a much higher flexural strength of 86.9 MPa than porous SiC ceramics without PHAS 14 MPa addition due to the enhancement of the neck growth by PHAS [19]
Kim <i>et al.</i>	Light weight pottery	Surface strengthening solutions (magnesium chloride, MgCl, aluminum nitrate hydrate, Al (NO ₃) ₃ ·9H ₂ O and potassium nitrate, KNO ₃)	Slip casting (surface infiltration)	First sintering at 900°C Final sintering at 1250°C	–	–	–	–	–	–	Ceramics soaked in 3 M Al solution for 5 s showed 30% higher levels of bending strength compared to ordinary light weight ceramics. This was due to the formation of the mullite phase For ceramics soaked in Mg solution, the bending strength increased with concentration and infiltration time. Bending strength increased to as much as 26% greater than the ceramics that had not been soaked in the strengthening solution [98]
Junkesa <i>et al.</i>	Alumina	Coating	Pre-ceramic papers (rolling)	1600°C	–	Stirring	Organic filler and cellulosic fibers	2 h	–	23–26%	The infiltration of the polysiloxane polymer into the paper-derived alumina substrates during coating was more effective in sealing the surface porosity when compared to the silica suspension The polysiloxane filled samples showed a higher mechanical strength (350 MPa) and lower water absorption than other ceramics due to the decrease in open porosity that coating with polysiloxane brings Higher mechanical strength was achieved when the open porosity was minimized [97]
Yao <i>et al.</i>	Si ₃ N ₄	Fabrication parameters (Si size, the Y ₂ O ₃ particle size, and second phase)	Powder metallurgy (dry pressing)	1860°C	10 MPa	Ball milling (24 h) in ethanol	–	2 h	–	42.14–46.54%	With the decrease of the particle size of Si, the microstructures become finer, the shrinkage increases gradually, the flexural strength is improved. Porosity of 42.14–46.54%, flexural strength of 141 MPa at to 165 MPa can be obtained

(Continued)

Table 7 Continued

Author	Work conditions								Major finding		
	Porous materials	Others factors	Method	Range of sintering temperature (final sintering)	Range of pressure (MPa)	Mixing method	Pore forming ratio (%) and size (μm)	Sintering time (soaking) time (h)	Pore size (μm)	Porosity ratio	Mechanical properties
Komlev <i>et al.</i>	Hydroxyapatite	Polymer impregnation (immersing in the polymer solution under a vacuum of 1.33 Pa for 10 or 30 min, and without vacuum for 30 min)	Powder metallurgy (dry pressing)	1200°C	50 MPa	Stirring	–	1 h	1–100 μm	45–50%	Using nano- Y_2O_3 as a sintering additive, it endorses the formation of fine $\beta\text{-Si}_3\text{N}_4$ grains. On the other hand, a high content of $\beta\text{-Si}_3\text{N}_4 > 20\%$ after nitridation also works as a nuclei location for precipitation and consumes a large amount of Si–N in the liquid phase. The growth of the fine $\beta\text{-Si}_3\text{N}_4$ grains is restrained. The improvement in flexural strength is minimized [95]. The samples infiltrated with 10% gelatin and 4% PVA solutions exhibit the maximum tensile strengths of 9.8 and 5.7 MPa, respectively; these values were reached if the infiltration was performed under vacuum at 1.33 Pa for 30 min [94].
Kawai <i>et al.</i>	Si_3N_4	Grain size distribution	Powder metallurgy	–	–	–	–	–	0.56–0.96 μm	27–43%	The strength of the porous Si_3N_4 ceramics does not always increase with the decreasing porosity and depends on the grain length of $\beta\text{-Si}_3\text{N}_4$; a longer grain leads to higher strength [93].
Zhu <i>et al.</i>	SiC reticulated porous ceramic (SiC RPCs)	Vacuum degassing	Polymeric sponge	1400°C	–	Ball milling (24 h)	Polyurethane sponge	3 h	100 μm	–	Vacuum degassing has a great effect on the mechanical properties of SiC RPCs prepared by the polymeric sponge process. Flexural strength of RPCs increases from 2.34 to 3.18 MPa after degassing. The increase in the relative density from 0.21 to 0.22 is also beneficial for increasing the strength [92].

density compared to 87.6% for the undoped ceramics. The hardness of Al_2O_3 containing up to 0.5 wt% CuO, for a sintering temperature of 1400°C , were higher ($\sim 14\text{--}17.1$ GPa) than those of the undoped ceramics ~ 12.4 GPa. In contrast, the hardness of the undoped Al_2O_3 increases with increasing sintering temperature, i.e., from 12.4 GPa at 1400°C to 21 GPa at 1600°C (see Fig. 59).

The lower hardness of the doped ceramics reported could be due to the increased grain size with increasing sintering temperature (see Fig. 60) [99].

Liu *et al.* [19] studied the effect of the oxidation degree for porous SiC ceramics with and without PHAS addition. The study showed that with increasing sintering temperature and oxidation degree, the flexural strength increases. In addition, the increase of the PHAS content (0–5%) promotes the oxidation of SiC from 24.88 to 43.79% and improves the strength of porous SiC ceramics from 14.07 ± 1.3 to 86.97 ± 10.2 MPa but causes the open porosity to decrease from 51.1 to 35.3% at a sintering temperature of 1450°C . The increasing trend in flexural strength was attributed to the acceleration of mullitization by the PHAS which encourages the development of the bonding necks between the SiC particles leading to a decrease in porosity. Zhang *et al.* [6] presented the effects of pre-oxidation on the microstructure and the mechanical properties of highly porous Si_3N_4 ceramics prepared via freeze casting and sintering. The study explained that the flexural strength of porous Si_3N_4 is strongly affected by the pre-oxidation temperature (see Fig. 23). The average flexural strength of the pre-oxidized specimens first increased from 33.5 to 34.2 MPa, then decreased from 34.2 to 14.2 MPa, and finally increased from 14.2 to 25.6 MPa at different sintering temperatures. These changes were due to the bonding necks among the particles, the oxidation degree of the Si_3N_4 , microcracks (mostly caused by cristobalite) and the porosity (see Fig. 61).

In addition, the solid content ratio is another factor reported by researchers as affecting the mechanical properties of porous ceramics. Ye *et al.* [100] studied the effect of solid content on the pore structure and the mechanical properties of porous Si_3N_4 ceramics produced by freeze casting. The porosity decreased from 66.3 to 42.7% and changed the pore structure from an aligned channel with dendrites to round pores (see Fig. 61), with increasing solid content from 30 to 50 vol%. The formation of these round pores obstructed the formation of the $\alpha\text{-Si}_3\text{N}_4$ phase, but it was found to be useful for improving the mechanical properties of porous Si_3N_4 ceramics because of its unique pore structure. The fracture toughness and the flexural strength of porous Si_3N_4 ceramics with a solid content of 50 vol% are $3.5 \text{ MPa}\cdot\text{m}^{1/2}$ and 189 MPa, compared with the 30 vol% when the values were $1.1 \text{ MPa}\cdot\text{m}^{1/2}$ and 57 MPa, respectively (Fig. 62).

Hou *et al.* [101] presented the effects of solid content on the mechanical properties of porous Y- α -SiAlON ceramics prepared by freeze casting. The results revealed that by increasing the contents of initial solid loading from 10 to 30 vol%, the average pore size decreased from 19 to 8 μm , the porosity decreased from 64.3 to 23.1%, the flexural strength increased significantly from 72.4 to 190.2 MPa and the fracture toughness increased from 1.20 to $3.48 \text{ MPa}\cdot\text{m}^{1/2}$. In general, the mechanical properties of porous ceramics were affected by the formation of a dense ceramic wall and the porosity. Fig. 63 shows full densification walls of porous Y- α -SiAlON ceramics without any defects or micro-pores in these walls, regardless of the initial solid loading. Therefore, they reported that the excellent mechanical properties are also attributed to the full densification Y- α -SiAlON ceramic walls.

Eom *et al.* [102] studied the effect of forming methods on the porosity and the compressive strength of polysiloxane-derived porous SiC ceramics using compression molding, injection molding, and extrusion processes. It was found the extrusion-molding leads to a higher porosity (84%) than the other forming processes (72–74%) as a result of the higher level of expansion of the expandable microspheres. In contrast, the compression molding process leads to a more homogenous microstructure than the other processes, resulting in an excellent compressive strength of 20.6 MPa at a porosity of 72.4%. Injection molding also leads to the partial segregation of the expanded microspheres, hence resulting in a moderate compressive strength of 9.1 MPa at 74.1% porosity. Heness *et al.* [103] reported the effect of specimen size on the compressive strength of porous alumina silicate insulating bricks. It was found that the strength of highly porous ceramics increases with the increasing volume of highly porous ceramics. Table 7 shows examples of other factors affecting the mechanical properties of some porous ceramic materials with different work conditions.

Conclusion

Many efforts have been made to improve the mechanical properties of porous ceramic. This review article has highlighted the factors affecting the porosity, the mechanical properties, and the strength of porous ceramics along with the microstructural factors.

The sintering temperature has a strong effect on the mechanical properties and the strength of porous ceramics. Increasing the sintering temperature also results in increased mechanical properties. The increase in the mechanical properties could be due to several factors, such as the grain structure (rigid honey comb and fibrous structure), the enhancement of the growth of necks, the improvement in densification, the homogeneity of pore distribution, the steps in the sintering process, and ceramic phase formation (mullite, cristobalite, $\beta\text{-Si}_3\text{N}_4$, etc.) after the sintering process and the decrease in the porosity.

A pore forming agent affects the mechanical properties with increasing ratio, the particle size of the pore forming agent, and the size, shape, channels, and distribution of the pores. As the porosity percentage increase, the mechanical properties decrease.

Ceramic additives have a significant effect on the mechanical properties of porous ceramics, affecting the accumulation of nanoparticles at the grain boundary, phase transformation, grain structure (sandwich structure, spot welding structure, pore channels, interlocking microstructure, bird's nest structure, etc.) and densification.

Metal particle additives also have important effects on the mechanical properties of porous ceramics. Increasing the metal particle content can improve the mechanical properties due to its effect on the sintering process, the crack bridging technique, the increased density, the decreased porosity, and the phase formation.

The mechanical properties of porous ceramics increase with decreasing particle size. This is related to the well-developed neck, the homogenous pore distribution and the decreased porosity. In addition, there are many different factors affecting the mechanical properties, such as the oxidation degree, coating, template size, specimen size, forming methods, solid contents, grain structure (dense ceramic wall structure), grain size distribution, and implantation time.

The ceramic materials used as porous ceramics in the selected papers studied have a different percentage ratio of SiC (94.74%), Si₃N₄ (73.68%), alumina (Al₂O₃) (42%), HAP (21%), mullite (15.8%), alumina–mullite (15.8%), mullite–SiC (15%), cordierite (10.52%), and spinal (10.52%), and the remainder of the porous ceramics are in the ratio of 5.26%, for example, clay, porcelain, cordierite–SiC, zirconia (ZrO₂), pottery, Y- α -SiAlON and bioactive glass.

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Ceramic Matrix Composites With Carbon Nanophases: Development, Structure, Mechanical and Tribological Properties and Electrical Conductivity

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Abbreviation

CCVD	catalytic chemical vapor deposition	FLG	few-layer graphene
CMC	ceramic matrix composite	FS	flash sintering
CNF	carbon nanofibre	GNP	graphene nanoplatelet
CNT	carbon nanotube	HIP	hot isostatic pressing
COF	coefficient of friction	HP	hot pressing
EDM	electric discharge machining	MLG	multi-layer graphene
EDX	energy dispersive X-ray spectroscopy	SEM	scanning electron microscopy
FAST	field assisted sintering technique	SPS	spark plasma sintering
		TEM	transmission electron microscopy

Introduction

Due to their strong interatomic bonds, ceramic materials are extremely durable and feature excellent properties, including relatively low density, very high hardness, strength, high temperature and chemical stability, corrosion and wear resistance. On the other hand, these bonds hinder their ability to plastically deform and tolerate defects, resulting in low fracture toughness and low crack propagation resistance, high brittleness and lower reliability.

Modern ceramic materials have achieved a significant improvement over traditional mainly due to the significant trend of minimization of the amount and the size of the defects (Morrell, 1985). This allows the increase of their strength and reliability. Further possibility for improving their performance lies in increase of their fracture toughness, which can be achieved by preparing a suitable microstructure, as well as, by combining the appropriate materials. This approach is therefore based on the specific design and preparation of ceramic matrix composites (CMCs) (Dusza and Šajgalík, 2009; Hvizdoš *et al.*, 2013b). Composite material is a mixture of two or more mutually insoluble materials or phases of the same material with properties superior to that of the component materials (Vencel *et al.*, 2004). In CMCs, the ceramic matrix is strengthened or toughened by the addition of secondary phases that allow slowing down or even arresting the crack growth by various micromechanisms, such as crack deflection and branching, or dissipation of fracture energy. Such secondary phases may have higher plasticity, e.g., in metal-ceramic composites (WC-Co), where a ductile metal phase gives the composite high toughness as well as electrical and thermal conductivity. This approach is very successful in practice. Its drawback is that it reduces the chemical and, in particular, the thermal resistance of the composite to a level corresponding to the metal component and it also increases the density (mass) of the composite.

Another approach uses non-metallic substances, which may not be inherently plastic, but may form suitable residual stresses, have higher strength, or be suitably shaped to contribute to the activation of toughening mechanisms. In the last two decades, such substances often take the form of particles or whiskers with high aspect ratio (Šajgalík *et al.*, 2000; Hvizdoš *et al.*, 1996; Hvizdoš and Dusza, 1998; Hvizdoš *et al.*, 2004). Recently, fibrous (1D) and flat (2D) structures have also become popular. Among the most promising candidates of this type are carbon-based structures, such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs). These structures have attracted great attention due to their extraordinary mechanical properties, thermal resistance, and useful electrical properties such as high electrical conductivity, all at their small size and low density.

High hardness and abrasion resistance of ceramic materials generally also mean relatively demanding shaping of finished products. If possible, the shape of the product is already determined during the initial molding. Indeed, sintered ceramics can usually be machined only with diamond tools and only to a limited extent. Such difficult-to-process and difficult-to-machine materials include the traditional silicon carbide (SiC) refractory, the modern ceramic silicon nitride (Si₃N₄), and the advanced ultra-hard boron carbide (B₄C) – three different non-oxide ceramics with a wide range of applications. All three are sintered at high temperatures, often using high pressures and various sintering additives. Thus, their final shaping is complicated by the complexity of their sintering (limited geometry in high pressure sintering), as well as the resulting properties. The SiC is a refractory, very hard and relatively brittle material, the Si₃N₄ is solid, durable and suitable for machine parts, whereas the B₄C is extremely hard and abrasion resistant. With such problematic machinability and the necessity of using almost exclusively diamond tools, the final cutting and grinding becomes economically disadvantageous.

An interesting alternative to diamond tooling, often used, for example, in machining carbides and metal matrix composites, is electric discharge machining (EDM). However, in order to be machined by the EDM, hard ceramic materials need to be electrically conductive. The Si₃N₄ is a typical insulator, whereas SiC and B₄C are normally semiconductors with relatively large band gaps

(3.2 and 2.09 eV, respectively). This feature allows them to be used in high-performance semiconductor devices (Kobayashi *et al.*, 2006). Since none of the three materials is DC conductive, in order to be able to use EDM, they must be treated by adding suitable electrically conductive improvers.

Thus, new CMCs with added CNTs and GNPs are being developed with respect to several goals:

- Improve the mechanical properties of ceramics through strengthening mechanisms;
- Develop the functionalized ceramics with improved magnetic and electrical properties;
- Use the acquired electrical conductivity to apply the new machining and shaping technologies for extremely hard and brittle ceramics.

State-of-the-Art

In recent years, with the advent of new materials based on pure carbon, great effort of material scientists have been devoted to experiments and research into their combination with more traditional materials of different properties. This includes the case of the ceramic matrix composites (CMCs) with carbon nanophase additions. Initially, relatively modest results were obtained in materials with CNT additions with a silicon carbide matrix (Ma *et al.*, 1998), followed by silicon nitride (Balázsi *et al.*, 2003; Belmonte *et al.*, 2010). Some papers have reported an improvement in fracture toughness of alumina matrix materials (Zhan *et al.*, 2003b; Puchý *et al.*, 2011), but quite often results in new composites have been disappointment, presumably due to difficulties in distributing CNTs in the ceramic microstructure and due to weak matrix/CNT bonds. Better results have been achieved in increasing the electrical conductivity of many, initially non-conductive, ceramics (Zhan *et al.*, 2003a; Balázsi *et al.*, 2006) and in improving tribological behavior of fragile material systems (Hvizdoš *et al.*, 2010; Gonzalez-Julian *et al.*, 2011, 2014; Belmonte *et al.*, 2013). After the emergence of graphene (Geim and Novoselov, 2007), whose preparation proved to be much easier in many respects than the preparation of CNTs (Zhu *et al.*, 2016), the work on its use to improve the properties of ceramics was relatively successful (Walker *et al.*, 2011; Ramirez *et al.*, 2011, 2012; Kun *et al.*, 2011; Kvetková *et al.*, 2012; Hvizdoš *et al.*, 2013b) regarding the enhancement of fracture toughness, abrasion resistance, and electrical conductivity. This section is devoted to the basic properties of silicon carbide, silicon nitride and boron carbide, as ceramic matrix materials, as well as to appropriate fillers (carbon nanotubes and graphene nanoplatelets). It provides basic information on the ongoing efforts to combine these materials to achieve better final material's performance.

Silicon Carbide (SiC)

Silicon carbide is a hard material that has been used in ceramic applications for a long time. It is also one of the mostly used reinforcing materials in metal matrix composites (Vencl, 2012). Its α -phase, stable to high temperatures, is crystallographically hexagonal, and is formed when carbon and silicon, in the form of various compounds, come into contact at high temperature in a reducing atmosphere. All crystalline SiC modifications have a binary tetrahedral structure – each silicon atom is surrounded by four carbon atoms and also each carbon atom by four silicon atoms. Thus, the structure consists of two identical, mutually overlapping, closely spaced Si and C layers which are displaced relative to each other in the direction of the c -axis by $1/4$ of the interlayer. The variability in the arrangement of these layers results in a number of forms in which SiC can occur. The theoretical density of SiC is 3.217 g cm^{-3} . However, the low energy difference in changing the sequence of layers leads to a huge variety of polytype formations. At present, their number exceeds 200. This polytypism does not affect the mechanical properties of SiC-based materials, but leads to high planar defect densities and mixed structural types. The irregularly curved SiC grain surface is a manifestation of layer defects and twins.

The high decomposition temperature (approximately 2700°C) makes it suitable as a material useful for bearings or furnace/heating elements. Its very low coefficient of thermal expansion ($4 \times 10^{-6} \text{ K}^{-1}$) with no phase transformations guarantees high thermal stability and thermal shock resistance. However, due to the high hardness (HV between 22 and 26 GPa), its machining is problematic. Almost exclusively diamond tools must be used for machining. Another complication is its low fracture toughness ($< 3 \text{ MPa m}^{1/2}$), which makes it very sensitive to the presence of defects. Therefore, various sintering additives, most often oxide-based (Falk, 1997; Kim and Kim, 1990; Misra, 1991), are used in the preparation of polycrystalline SiC, making it possible to obtain dense microstructures without pores and other critical defects. This allows for higher strength values while maintaining the fracture toughness constant.

An increase in fracture toughness have been achieved by changing the sintering technology where β -SiC is converted to α -SiC, which forms large platelet grains, by phase transformation in the process of preparation. Their presence in the microstructure of the dense material results in deflection and bridging of any propagating crack, thereby dissipating its energy and inhibiting its growth. Such procedures have improved fracture toughness to values of about $8 \text{ MPa m}^{1/2}$ (Moberlychan *et al.*, 1998; Padture, 1994). Another approach to overcome brittleness of SiC is to improve its mechanical properties by adding metal particles (Petit *et al.*, 2002; Peng *et al.*, 2004; Raddatz *et al.*, 2000). This trend of production of ceramic-metal composites (cermets) has brought the ability of the material to bear higher loading due to the presence of a tensile (metal) phase. Mastering the preparation of SiC-based cermets has brought some improvements in mechanical properties, but the possibility of increasing their conductivity through this path is still relatively less explored (Janz *et al.*, 2006; Duan *et al.*, 2004; Zhang *et al.*, 2004), even though it offers wide possibilities of utilizing not only mechanical but also functional properties of SiC. In this way, the self-diagnosis could be used to monitor the

condition of the component and its structural integrity, or to control conductivity, etc. However, the temperature resistance is limited by the resistance of the present metal phase.

Silicon Nitride (Si_3N_4)

Silicon nitride does not occur as a natural substance. It is a human-synthesized compound using a series of chemical reactions. The products are pressed and sintered into a final bulk ceramic having a unique set of excellent properties. As ceramics, silicon nitride has a relatively high strength and fracture toughness, low density (around 3.2 g cm^{-3}), due to the SiO_2 surface layer good corrosion and oxidation resistance at room and elevated temperatures. Due to its low thermal expansion coefficient ($3.1\text{--}3.6 \times 10^{-6} \text{ K}^{-1}$ from room temperature up to 1000°C) it also has a relatively good resistance to temperature shocks (Morrell, 1985).

Silicon nitride cannot be sintered directly since it decomposes above 1850°C at a pressure of 0.1 MPa. One of the commonly used methods for the preparation of Si_3N_4 bulk ceramics is the reaction sintering, resulting in, so-called, reaction bonded silicon nitride (RBSN). This method is based on heating the silicate compacts under a nitrogen atmosphere. The resulting material usually has a higher open porosity. Fully dense materials are prepared by hot pressing (HP) or hot isostatic pressing (HIP) at temperatures from 1700 to 1800°C , using oxides as sintering additives that form liquid phases during sintering. The microstructure of the resulting materials consists of fine grains of $\alpha\text{-Si}_3\text{N}_4$ and larger $\beta\text{-Si}_3\text{N}_4$ grains with higher aspect ratio. Such a microstructure is desirable as it is characterized by higher strength and improved fracture toughness.

Silicon nitride is a relatively expensive material. However, in applications where its excellent properties are combined with its durability and low maintenance, it can also be economically advantageous as it has excellent abrasion and erosion resistance. High quality silicon nitride based materials have been developed for use in combustion engine valves and cams where they have proven themselves very well. The cost of larger ceramic parts has never fallen enough to be used to produce all-ceramic engines or turbochargers. Nonetheless, high quality components can be manufactured and used in many applications under high mechanical or thermal stress or abrasion conditions.

Boron Carbide (B_4C)

Boron carbide was discovered in 1858 as a by-product of chemical reactions with metal carbides. Its exact stoichiometry was identified only in 1934. It is an extremely hard material. In fact it is the third hardest bulk substance known to mankind after diamond and cubic boron nitride with hardness $\text{HV} = 34 \pm 4 \text{ GPa}$ and Young's modulus of $360\text{--}460 \text{ GPa}$ (Sairam *et al.*, 2012). Its melting point is 2450°C and thermal conductivity $30 \text{ W m}^{-1} \text{ K}^{-1}$. It is a semiconductor with energy band gap depending on dopants/impurities and the degree of order. The average is estimated at 2.09 eV (Domnich *et al.*, 2011). Thanks to its exceptional properties, it is used or considered as a good candidate for aerospace materials, lightweight armors and bullet-proof tiles, nuclear control rods and absorbers, neutron shields, wear resistant components, etc. (Thévenot, 1990; Sedláč *et al.*, 2017).

Carbon Nanotubes (CNTs) and Graphene Nanoplatelets (GNPs)

The basic structural unit of both carbon nanotubes and graphene nanoplatelets is the graphene plane. The graphene plane can be defined as a hexagonal network of covalently bonded carbon atoms, or as a single two dimensional (2D) one atom thick monolayer (Fig. 1(a)), which is the basic building block of three-dimensional (3D) graphite. Simply twisting the graphene plane into a cylinder, single-wall carbon nanotube (SWCNT) is formed (Fig. 1(b)), which may have different radii. If one plane twists into a spiral, or multiple planes nest inside one another, a more frequent structure is created – multi-wall carbon nanotube (MWCNT), Fig. 1(c). The nanotubes have a diameter of a few nanometers but usually a length in micrometers or more. Their unique structure results in extraordinary features that have made them extremely popular candidates for materials of the future (Iijima, 1991).

High quality single-walled (or few-walled) carbon nanotubes have an extremely large length-to-diameter (aspect) ratio, since their diameter can be just a few nanometers. The CNTs are therefore the strongest known material with a specific strength reaching 100 times

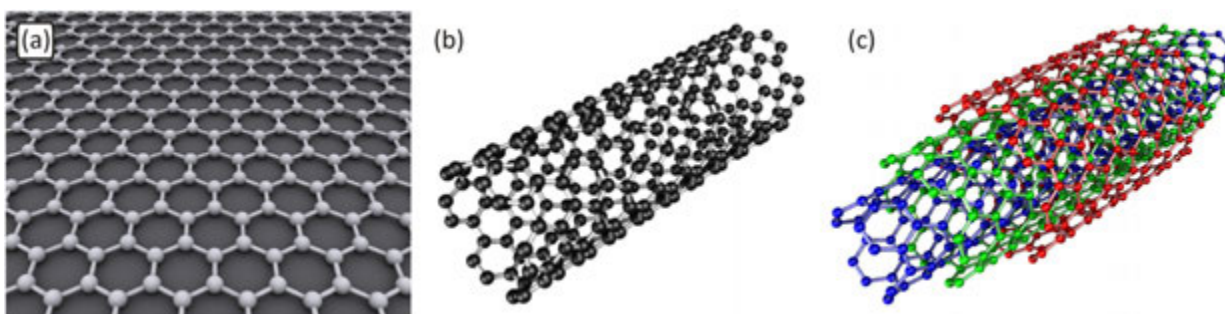


Fig. 1 Schematic representation of the carbon nanostructures: (a) graphene monolayer, (b) single-wall nanotube (SWCNT) and (c) multi-wall nanotube (MWCNT). Source: Wikipedia.

that of steel. For the single-walled CNTs, the strength values range from 50 to 200 GPa, the Young's modulus is about 1 TPa, and their fracture deformation is between 5% and 20%. Due to their size and high degree of crystalline perfection, CNTs can be defect-free, achieving extraordinary strength. Despite their exceptional mechanical properties, SWCNT are not used very often as reinforcing elements, because their preparation is very demanding and expensive. On the other hand, the preparation of the multi-walled ones is much simpler. The MWCNTs usually contain concentric graphene monolayers and have a diameter of the order of tens of nanometers depending on the layer number. The disadvantage is that these structures can fail by a "telescopic" mechanism, as the individual graphene layers relatively easily slip. This property, together with the greater probability of structural defects, is a disadvantage compared to SWCNT, but they can still overcome common structural materials in terms of strength and modulus of elasticity.

Graphene has similar electrical, mechanical and thermal properties to CNT (Geim and Novoselov, 2007). Compared to nanotubes, the main advantage of graphene is its larger surface area and lower tendency to agglomerate, making it easier to achieve a good dispersion in the matrix. Its preparation is also simpler and usually cheaper. For example, it can be prepared by simple mechanical exfoliation, so it is potentially easier to use in practice (Zhu *et al.*, 2016; Kun *et al.*, 2011).

Strictly speaking, graphene refers to a pure monolayer of carbon atoms arranged in a hexagonal lattice with sp^2 bonds (Fig. 1(a)). This structure has unique electronic, elastic, mechanical and thermal properties (Geim and Novoselov, 2007). Graphene is the first example of a truly two-dimensional crystal. Its preparation in larger quantities is still not a matter of routine. This is why attention has been recently paid in particular to multi-layered graphene nanomaterials mainly due to the considerably lower cost of preparation while preserving the exceptional mechanical and electrical properties (Bianco *et al.*, 2013; Wick *et al.*, 2014). These nanomaterials are known as "few-layer graphene" (FLG), "multilayer graphene" (MLG), or "graphene (also called graphite) nanoplatelets" (GNP). They consist of a series of graphene monolayers, 2–5 for FLG, less than 10 for MLG and above 10 for GNP. They are well ordered structures with a total thickness below 100 nm. These types also differ in the average lateral size and in the typical carbon-oxygen ratio (Jang and Zhamu, 2008; Wick *et al.*, 2014). Since graphene monolayers are known for their exceptional electrical properties with extremely high electron mobility at room temperature (like CNTs), the incorporation of GNP as a filler into ceramic matrix composites could be an economically advantageous alternative that would lead to high utility materials with improved electrical properties (Miranzo *et al.*, 2017).

Depending on the CNT chirality, the electrical conductivity of the individual nanotubes may be of metallic or semiconductor type, with the axial component being extremely high, $2 \times 10^7 \text{ S m}^{-1}$ (Ebbesen *et al.*, 1996), comparable to that of silver, copper, or gold. The conductivity of the graphene layers is similar to that of the CNT, as it is the same mechanism of charge carrier mobility. In practice, it is limited by the phonon scattering and is dependent on their chemical and structural purity.

Preparation and Characterization of Composites With Carbon Nanophases

This section describes a set of experimental materials: composites based on silicon nitride, silicon carbide and boron carbide, all with addition of carbon nanophases. Further, it describes the methods of characterization used in the research, development and optimization of the materials in question.

Composites With Carbon Nanophases

Design and manufacturing of the composite materials with matrices of SiC (SiC-CNT, SiC-GNP), Si_3N_4 (Si_3N_4 -CNT, Si_3N_4 -GNP), and B_4C (B_4C -GNP) were mainly based on typical advanced ceramics sintering, i.e., hot pressing (HP) or hot isostatic pressing (HIP). Where appropriate, the possibility of using new methods based on field assisted sintering techniques was explored, such as pulsed electric current sintering (PECS), spark plasma sintering (SPS), flash sintering (FS), which are fast and able of preserving a fine-grained matrix, carbon nanostructures (their decomposition can be avoided), and also economic benefits due to very short times and energy savings. At the same time, non-traditional methods of preparing composite fillers, such as the formation of CNT in-situ on the surface of ceramic powder particles by CCVD were also investigated.

SiC-CNT

In the past, many studies showed the difficulties in good distribution of CNTs due to their strong tendency to agglomeration. In the case of the preparation of SiC-CNT composites, the techniques of their growth directly on the surface of the ceramic particles in-situ using catalytic CVD (CCVD) have been successfully used to avoid these distribution and aggregation problems of pre-prepared and mixed nanotubes. This procedure provides a high degree of quality control and scalability (Jourdain and Bichara, 2013).

Džunda *et al.* (2019) used CCVD. They prepared a starting mixture of SiC powders with AlN and Y_2O_3 as sintering additives to which $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was applied. After mixing and drying, calcination at 750°C for 1 h took place in an Ar + H_2 atmosphere, which caused the nitrate to decompose and to form α -Fe nanoparticles on the SiC surface (Fig. 2(a)). This was followed by a pyrolysis at 700°C for 20 min, in a C_2H_2 + Ar + H_2 atmosphere. During this process atomic carbon was deposited on the ferrous precursor nanoparticles. The result was carbon nanotubes with high quality and excellent distribution grown directly on the surface of individual SiC powder grains (Fig. 2(b)).

The prepared powder mixtures were sintered at 1850°C , under Ar, for 60 min, at 30 MPa. Three SiC-CNT composites were prepared. The amount of CNT produced is quite difficult to control, so the materials are labeled according to the volume fraction

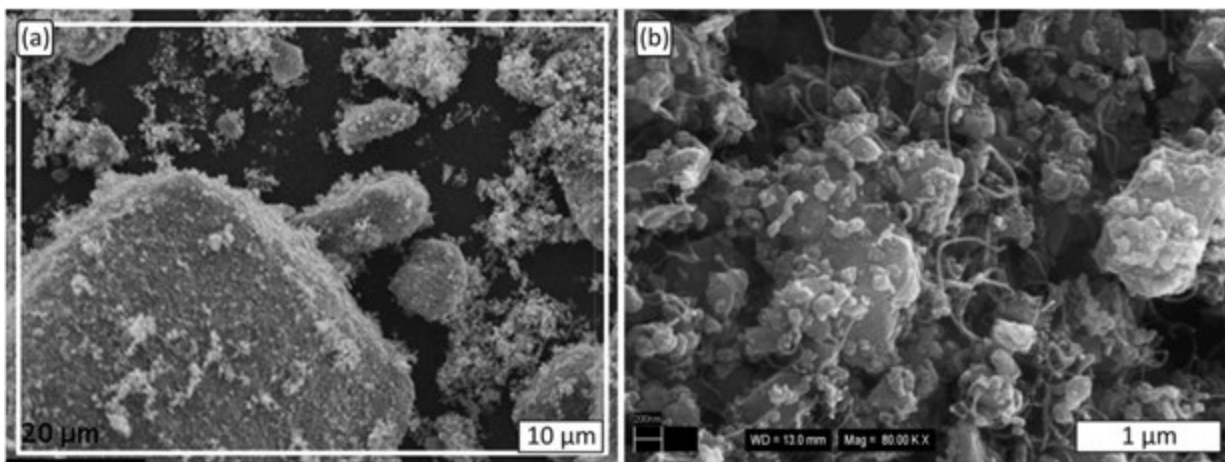


Fig. 2 Preparation of SiC–CNT by CCVD: (a) calcination of $\text{Fe}(\text{NO}_3)_3$ nanoparticles on the surface of SiC powder grains ($750^\circ\text{C}/1\text{ h}$, $\text{Ar} + \text{H}_2$ atmosphere) and (b) pyrolysis and SiC–CNT powder mixture after CCVD ($700^\circ\text{C}/20\text{ min}/\text{C}_2\text{H}_2 + \text{Ar} + \text{H}_2$ atmosphere). Reproduced from Džunda, R., Fides, M., Hnatko, M., *et al.*, 2019. Mechanical, physical properties and tribological behavior of silicon carbide composites with addition of carbon nanotubes. *International Journal of Refractory Metals and Hard Materials* 81, 272–280.

of Fe catalyst: C2 (2 wt% Fe), C5 (5 wt% Fe), and C10 (10 wt% Fe). Subsequent analyzes showed that the fraction of CNT approximately corresponds to the fractions of added Fe particles. At the same time, a reference sample of SiC–Fe was prepared where the CCVD final step was omitted, so that it contained Fe but no CNTs. This sample was labeled C0. Microstructure observations demonstrated excellent CNT quality and distribution.

SiC–GNP

In the case of SiC composites with graphene nanoplatelets, usually the standard mixing of the commercially available powders has been used. In the study of [Hvizdoš *et al.* \(2017\)](#), the starting powder was SiC labeled UF-15, from H.C. Starck (Germany), with a particle size of 550 nm. The graphene addition was commercially available nanofibers Gn(12), from Graphene Laboratories (USA), in amounts from 0 to 6 wt%. These materials were mixed for 2 h in an isopropanol rotary-vibrating mill using SiC beads as grinding media. Prepared mixtures were hot pressed at 25 MPa on 2100°C for one hour in an argon protective atmosphere ([Hvizdoš *et al.* \(2017\)](#)), similar to other studies ([Llorente and Belmonte, 2018](#); [Román-Manso *et al.*, 2016](#)), where sintering in SPS was included as the last step.

Si_3N_4 –CNT

The preparation of silicon nitride based composites with carbon nanotubes by the mixing of both components (and other necessary sintering additives) is a technologically rather demanding process to which researchers approach differently.

[Tatami *et al.* \(2005\)](#) used high purity and very fine grained Si_3N_4 together with Y_2O_3 , AlN, and TiO_2 as sintering additives. The MWCNTs were added as an electrically conductive phase. The proportion of CNT ranged from 0 to 12 wt% of the total amount of input powders. They used ethanol as the dispersant, with ratio of ethanol/CNT = 63/1, prepared as a suspension in an ultrasonic vibration stirrer. The prepared suspension was mixed with a mixture of Si_3N_4 – Y_2O_3 – Al_2O_3 –AlN– TiO_2 and further milled in a ball mill. After stirring, the ethanol was evaporated and the mixture was sieved. The product was isostatically cold pressed at 200 MPa. The green bodies were sintered under nitrogen at 1800°C for 2 h at pressure of 0.9 MPa. To increase the density, hot isostatic pressing (HIP) was used at 1700°C for 1 h at 100 MPa.

The alternative of growing CNT in-situ on Si_3N_4 grains was also explored. In some studies ([Berlanga *et al.*, 2011](#); [Gonzalez-Julian *et al.*, 2014](#)), the starting ceramic powder was ultrasonically mixed in methanol with a double-cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) used as a catalyst precursor for 15 min. The amount of CNT grown was controlled by a change in the fraction of cobalt in Si_3N_4 . The mixture was dried overnight at 125°C and sieved by a 63 μm mesh. The CNT synthesis took place in a modified tubular furnace equipped with a stirrer. The CVD process ran at 750°C for 15 min by thermal decomposition of the acetylene precursor with the addition of hydrogen as process gas. Finally, the powder was heated in air at 300°C for 30 min to remove residual amorphous carbon and re-sieved through a 63 μm mesh.

In other works ([Balázs *et al.*, 2004](#); [Hvizdoš *et al.*, 2011, 2012](#)), the initial powder mixtures of 90 wt% Si_3N_4 –4 wt% Al_2O_3 –6 wt% Y_2O_3 with addition of experimentally prepared MWCNT. These MWCNTs were synthesized in-house by the acetylene catalytic decomposition method on the Co/Fe catalyst. The resulting nanotubes were purified by stirring in concentrated hydrochloric acid for 5 h to remove the metal residues. They were then rinsed and added to the silicon nitride powders. The powder mixtures were subsequently milled for several hours in ethanol in an Al_2O_3 planetary mill as a grinding medium. After grinding, the mixtures were

still sonicated in an ethanol bath. Samples were compressed at 220 MPa. The green bodies were then sintered in BN powder bed at 1700°C in a high purity N₂ atmosphere using a two-step sinter-HIP method.

Si₃N₄-GNP

Following the experience of using CNTs, graphene structures, especially in the form of multi-layered GNPs, have become the focus of interest as a reinforcing additive, mainly due to their lower cost, easier preparation, and ease of use (Belmonte *et al.*, 2013). In the reviewed studies (Kvetková *et al.*, 2012; Hvizdoš *et al.*, 2013a; Balko *et al.*, 2014), the commercial products of XG Sciences (USA) and Angstrom Materials (USA), or laboratory prepared GNPs (Kun *et al.*, 2011), were successfully used. Mixtures containing 0–3 wt% GNP were mixed in an attritor at 600 rpm for 30 min. After mixing, they were dried and sieved through 150 µm sieves. Semi-finished products were cold pressed from the prepared mixtures at 220 MPa. These were then HIP at 1700°C in a high purity nitrogen in BN powder bed at 20 MPa for 3 h.

B₄C-GNP

The B₄C is a material difficult to sinter. In order to improve its densification at lower temperatures and to enhance its fracture resistance, strength and also to promote electrical conductivity, various additives have been tried, mostly carbon, boron, alumina, silicon, TiB₂, SiC, etc. (Kim *et al.*, 2000; Sedlák *et al.*, 2017). The material was prepared usually by hot pressing of very fine grain powders (< 2 µm) at high sintering temperatures of 2100–2200°C, heating/cooling rates 10°C min⁻¹ with typical dwell time 15–45 min under pressures 30–40 MPa. When graphene based nanostructures have attracted more interest, they were adopted for the use as fillers. To preserve their integrity, fast sintering methods were widely explored, such as spark plasma sintering (SPS) and flash sintering (FS) (Rehman *et al.*, 2014; Sedlák *et al.*, 2017, 2019).

Sedlák *et al.* (2017, 2019) performed a series of experiments and made a comprehensive comparison of B₄C-GNP composite prepared by hot pressing (HP), SPS, and FS. They used commercially available starting powders: B₄C grade HD 20 powder from H.C. Starck (Germany), with grain size 0.9–1.5 µm and nominal impurities (C:21.8, N:0.7, O:2.6, Fe:0.1, Si:0.15, Al:0.05); Gn(12) from Graphene Laboratories (USA), with average thickness of GNPs of 12 nm (30–50 monolayers). These powders were homogenized by simple mixing. The densification was performed by: hot pressing (2100°C/dwell time 1 h/25 MPa/Ar flow/10°C min⁻¹), spark plasma sintering (2200°C/dwell time 1–5 min/15 MPa/in vacuum/100°C min⁻¹) and flash sintering (2330–2450°C: estimated, since it is difficult to control, i.e., only by the electric power output/sintering 24 s/16 MPa/in vacuum).

The interesting thing was the total time of the procedure, which for HP was 7.5 h, for SPS it was about 1 h, and for FS it was within one minute only. In all cases the final materials contained between 0 and 6 wt% GNPs.

Methods of Characterization

Microstructural examinations

Microstructure of the prepared bulk composite materials was observed by high resolution SEM and TEM. SEM observations were made on samples that were cut and ground using diamond tools and polished to a roughness *Ra* of less than 100 nm. The polished surfaces were usually thermally etched to enhance grain structure, topography and distribution of composite phases. In some cases, fracture surfaces were observed to obtain information about the spatial character of the microstructure, as well as the cohesive and hardening mechanisms acting between matrix grains and the filler particles that determine the type of failure and the crack propagation.

The phase composition of the final composite materials was usually determined by X-ray diffraction, optionally supplemented with Raman or EDX spectroscopies.

Mechanical testing

The mechanical behavior was usually determined by the basic mechanical properties of bulk composites, such as hardness and indentation toughness, and measured by indentation methods. Hardness (HV) was measured by the Vickers method.

Fracture toughness (*K_{IC}*) was determined in most cases by the indentation method, as experimental materials were not available in the form of standard bars. Indentation toughness was measured using the relationship of Anstis *et al.*, (1981) for semi-elliptical indentation cracks:

$$K_{IC} = \eta F(E/H)^{1/2} / c^{3/2} \quad (1)$$

where η is the geometric factor, F is the peak load, E is modulus of elasticity, H is hardness expressed as the mean pressure in the indenter contact area (i.e., in Pa), and c is the indentation radial crack length measured on the surface from the middle of the imprint.

In some cases, it was also possible to measure fracture toughness using standardized notched bars (single edge V-notch beam test – SEVNB). In these cases, bending strength of 25 × 2 × 1.5 mm bars in a four-point or three-point bending was also tested. Inner/outer spans were 8/16 mm and the crosshead speed was 0.5 mm min⁻¹. Due to the limited number of samples, it was not possible to perform a full Weibull statistic, so averages of at least four measurements were given as strength values together with standard deviations.

Tribological testing

Tribological behavior of the experimental materials was observed in dry sliding conditions. As a rule, the tests were performed using the ball-on-disc method. The counter-bodies were spheres made of SiC and Si₃N₄ (according to the corresponding matrix material of the composite being tested) with a diameter of 6 mm. Their initial roughness was less than 1 μm. Sample surfaces were carefully prepared by polishing to a surface roughness of *Ra* less than 100 nm. During the tribological test, the tangential forces are continuously measured, so the friction coefficient values are calculated and recorded. On the basis of microscopic observations of tribological tracks, wear regimes and damage micromechanisms were determined. The specific wear rate (W_s) was calculated according to ISO 20808 standard:

$$W_s = V / (LF_p) \quad (2)$$

where V is wear volume loss, L is sliding distance, and F_p is applied normal load.

The phase stability of both ceramic matrices and carbon nanophases was determined by X-ray microdiffraction and Raman spectroscopy (Balko *et al.*, 2014). In some cases, the wear debris were also collected from the contact zone and their composition was identified by the diffraction of the synchrotron X-ray radiation to determine possible phase transformation of Si₃N₄ fragments at high temperatures (Balko *et al.*, 2014).

Electrical conductivity examinations

Electrical conductivity measurements were made at room temperature and ambient air humidity. Two-point or four-point impedance analysis was used on bar specimens at frequencies ranging from 42 to 40 kHz. For the thin flat samples, usually flat disks prepared by SPS, the four-point method of Van der Pauw (1958) was used.

Properties of Composites With Carbon Nanophases

Microstructure

As mentioned before, a great challenge for composites containing long fibers remains to achieve their good distribution and suppress the tendency to agglomeration and clumping. In the SiC–CNT experimental materials, the distribution of nanoparticles was very good when they were grown directly on the grain surface using CCVD (Džunda *et al.*, 2019). After the final compacting, the CNTs were evenly distributed in the resulting composites as illustrated for the case of the composite C2 in Fig. 3. All the samples had a bimodal SiC grain distribution consisting of fine polyhedral particles (size < 1 μm) and larger elongated grains with aspect ratio of about 3, with mixed CNTs of 10–50 nm in diameter. The main growth mechanism of the elongated SiC grains was the partial transformation of β-SiC to α-SiC as shown by XRD. In all cases with CNT present, the densities achieved were about 3 g cm⁻³, i.e., ~95%, which shows that full densification remains a challenge in these materials, as some porosity persisted.

In accordance to previously mentioned assumptions, the handling of GNPs was found to be simpler. In SiC matrix composites, the GNPs were well distributed in the microstructure after the hot pressing. They were, however, preferentially oriented in a direction perpendicular to the pressing direction (Fig. 4(a)). They were very well integrated into the matrix with solid bonds to SiC grains (Fig. 4(b)). In these composites, thin SiC grains and residual porosity were also seen, especially in materials with higher GNP contents (2, 4, and 6 wt%), Fig. 5.

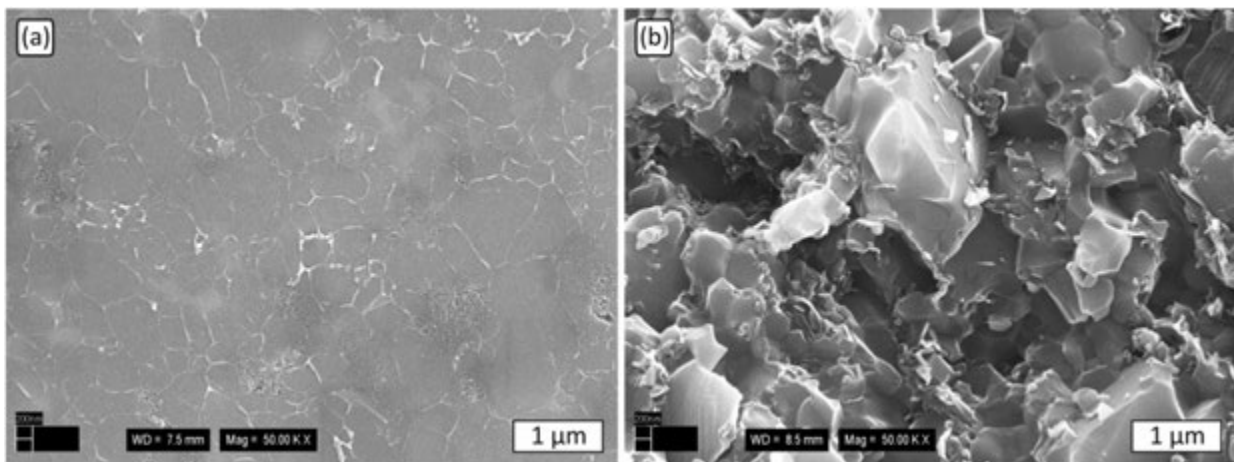


Fig. 3 Microstructure of the SiC–CNT composite: (a) plasma etched surface and (b) fractured surface. Reproduced from Džunda, R., Fides, M., Hnatko, M., *et al.*, 2019. Mechanical, physical properties and tribological behavior of silicon carbide composites with addition of carbon nanotubes. *International Journal of Refractory Metals and Hard Materials* 81, 272–280.

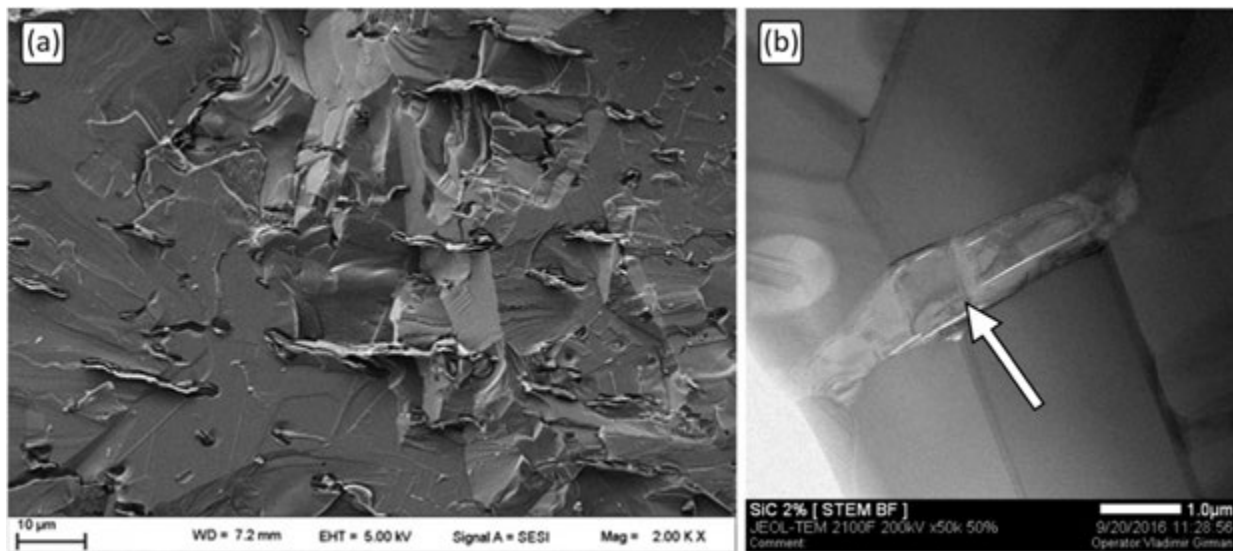


Fig. 4 Microstructure of the SiC-GNP composite with 2 wt% GNPs: (a) fractured surface illustrating the distribution and preferential orientation of GNPs and (b) TEM micrograph illustrating good integration of a GNP (denoted with arrow) into the SiC matrix. Reproduced from Hvizdoš, P., Fides, M., Kovalčíková, A., *et al.*, 2017. Electrically conductive SiC based composites – Development, microstructure, mechanical, electrical and tribological properties. In: Book of Abstracts of the Polish-Slovak-Chinese Seminar on Ceramics. Zakopane, Poland, pp. 74–75.

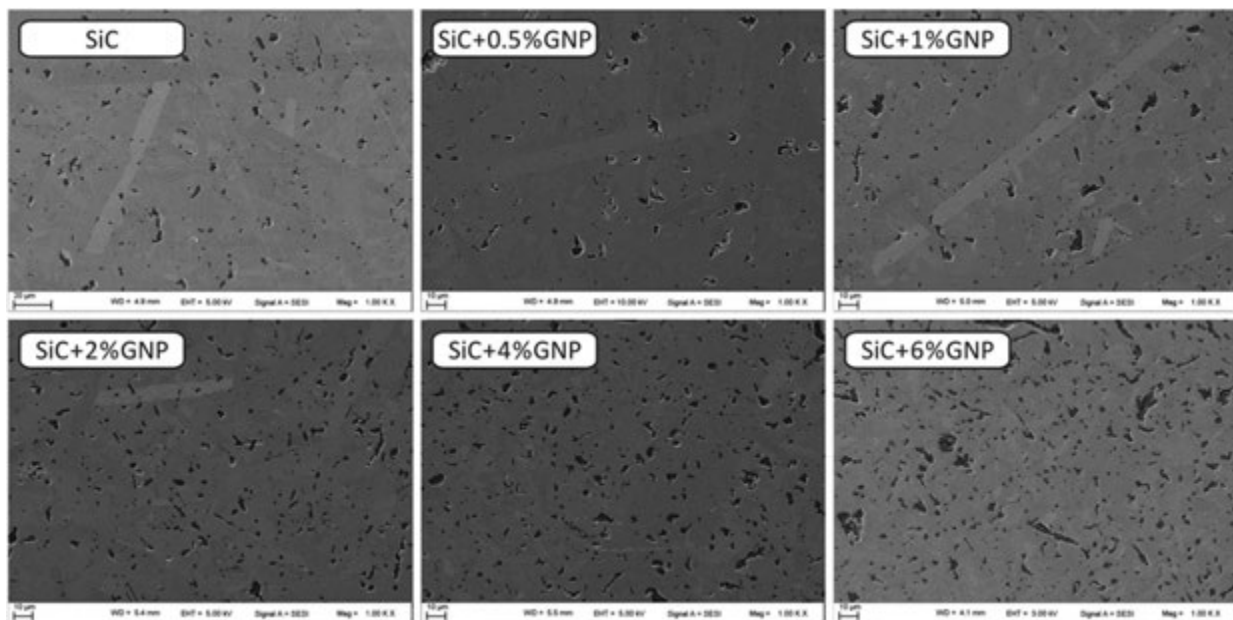


Fig. 5 Microstructure of SiC-GNP composites with GNPs illustrating the presence of elongated thin SiC grains and the residual porosity. Reproduced from Hvizdoš, P., Fides, M., Kovalčíková, A., *et al.*, 2017. Electrically conductive SiC based composites – Development, microstructure, mechanical, electrical and tribological properties. In: Book of Abstracts of the Polish-Slovak-Chinese Seminar on Ceramics. Zakopane, Poland, pp. 74–75.

Balázsi *et al.* (2006) and Hvizdoš *et al.* (2011, 2012) developed composites with a silicon nitride matrix and the addition of carbon nanotubes (Si_3N_4 -CNT) using hot isostatic pressing (HIP). These materials were compared with monolithic silicon nitride as well as composites with analogous amounts of pure carbon additive, but in the form of carbon black, prepared in the same way. Composites with 1, 3 and 5 wt% of multi-wall carbon nanotubes (MWCNT) were designed. All of these materials were carefully mixed, pre-pressed at room temperature under pressure of 200 MPa and subsequently HIP at 1700°C for 3 h at 2 MPa and 20 MPa. The CNTs were also found to be successfully preserved in the final structure. Problems with nanotubes degradation, which were recorded in earlier works (Balázsi *et al.*, 2003, 2004), have been removed in newer procedures (Hvizdoš *et al.*, 2012). The CNTs were mainly located in intergranular spaces with good bonding to silicon nitride grains, possibly even among themselves.

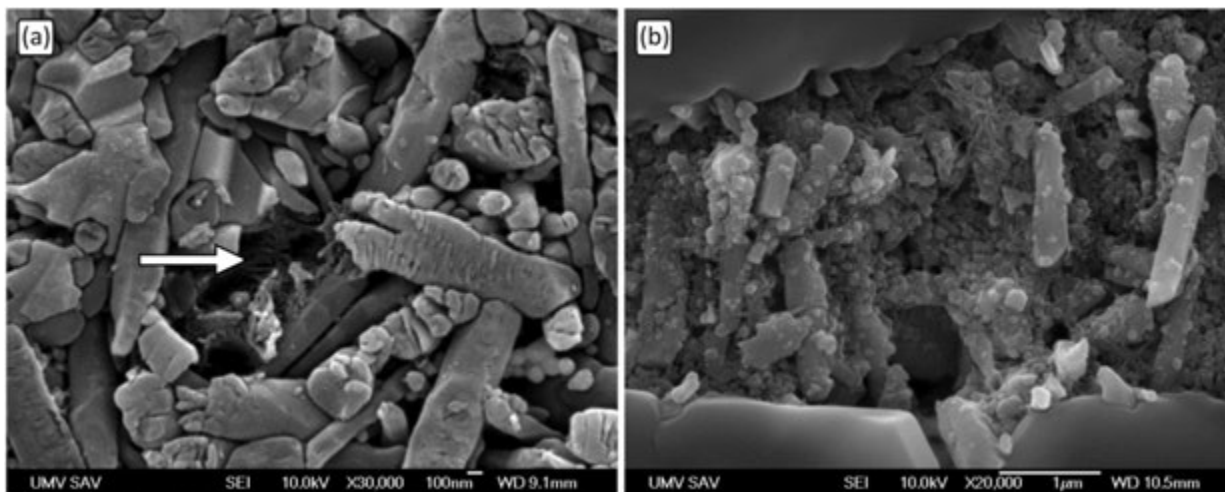


Fig. 6 Microstructures of Si_3N_4 -CNT composites: (a) nanotube clumps and islets (denoted with arrow) in Si_3N_4 + 1% CNT and (b) larger amounts of CNTs in Si_3N_4 + 5% CNT. Reproduced from Hvizdoš, P., Puchý, V., Duszová, A., Dusza, J., Balázsi, C., 2012. Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. *Ceramics International* 38, 5669–5676.

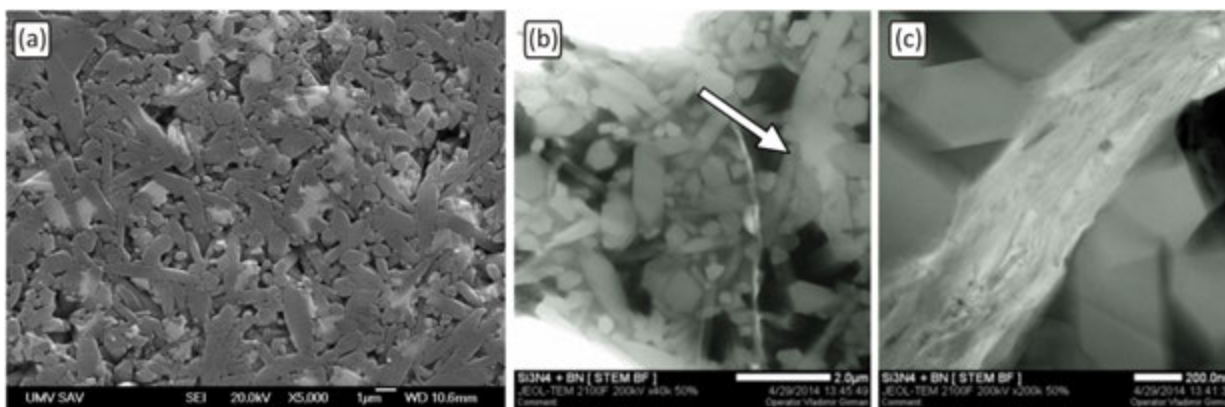


Fig. 7 Microstructure of Si_3N_4 -GNP composite with 3 wt% GNPs: (a) SEM image showing residual porosity, (b) TEM photograph illustrating incorporating of GNP between the matrix grains and (c) detail of a GNP within the matrix. Reproduced from Hvizdoš, P., Balko, J., Kovalčíková, A., Fides, M., 2015. Tribological properties of silicon nitride based composites with graphene and boron nitride nanoparticles. In: Abstracts of the First Polish-Korean Joint Workshop on Advanced Ceramics, p. 28. Zakopane, Poland.

However, the high quality CNTs separation and dispersion is still a challenging task in the preparation of the composite. In most cases, after milling (in ball or planetary mills), ultrasonic mixing is included to obtain better homogeneity of the powder mixtures. The increase in mixing time brings some improvement, but the tendency to agglomeration and entanglement, especially in nanotubes, is unlikely to be completely suppressed. In most cases of such preparation, the CNTs remained in groups as nano- or micrometric islets in the matrix even in the final material after sintering, **Fig. 6**. A different microstructure was achieved by increasing the pressure from 2 to 20 MPa and sintering time to 3 h. Grain growth accompanied by phase transformation was observed in composites with 1 and 3 wt% CNT, forming large β - Si_3N_4 grains. In general, samples with CNT addition had a significantly higher porosity than the reference samples.

In the silicon nitride – graphene composites, some residual porosity was associated with the added graphene nanoplatelets (GNPs). On the other hand, GNPs distribution was very good, and GNPs were suitably incorporated into the composite matrix (**Fig. 7**). The rare clusters of GNPs had properties different from that of typical CNT clusters. The GNP clusters did not have a globular shape, and usually contained only two or a few parallel nanoplatelets. Most often, however, individual GNPs were located at grain boundaries.

In B_4C -GNP materials prepared by HP and SPS the final densities were about 99% and more, showing very consistent behavior also for high amounts of GNPs. Flash sintering achieved densities from 91% to 95%, when higher amount of carbon actually led to higher density showing the benefit of densification promoting role of carbon. In all cases GNPs have preferential directionality because in all methods one axis pressing is used, but the integration into the matrix is excellent, **Fig. 8**.

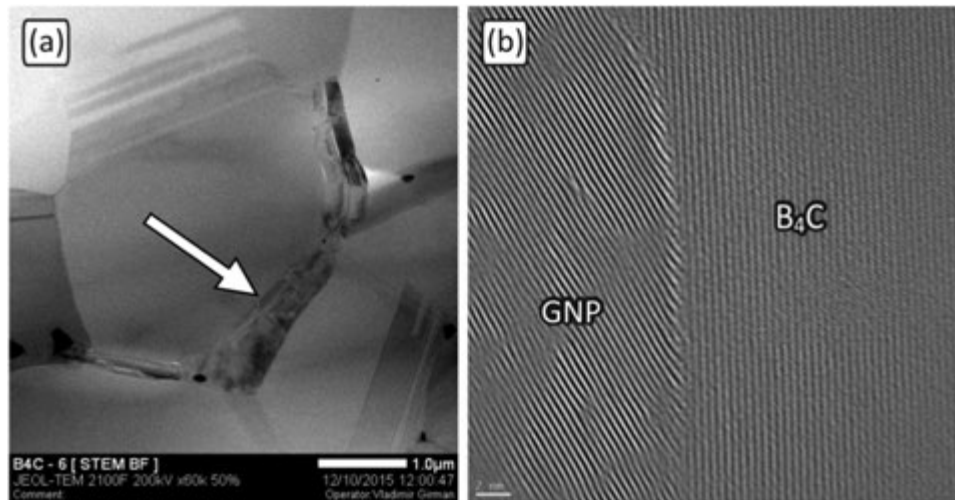


Fig. 8 TEM micrographs of B₄C–GNP composite: (a) intergranular integration of a GNP in B₄C + 6% GNP and (b) clean boundary between B₄C and GNP in B₄C + 4% GNP. Reproduced from Sedlák, R., Fides, M., Hvizdoš, P., *et al.*, 2019. Boron carbide based ceramic composites prepared by SPS and flash sintering. In: Extended Abstracts of the 11th International Conference on the Science of Hard Materials (ICSHM11), pp. 155–156. Khao Lak, Thailand.

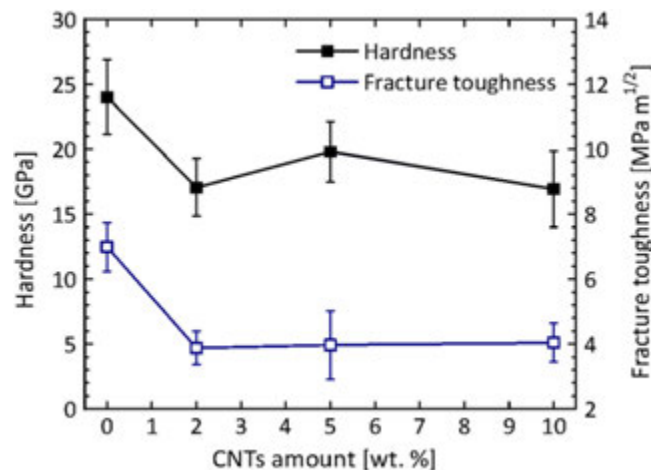


Fig. 9 Influence of the CNTs amount on hardness and fracture toughness of SiC–CNT composites. Reproduced from Džunda, R., Fides, M., Hnatko, M., *et al.*, 2019. Mechanical, physical properties and tribological behavior of silicon carbide composites with addition of carbon nanotubes. *International Journal of Refractory Metals and Hard Materials* 81, 272–280.

Mechanical Properties

Although the primary reason for introducing carbon nanotubes into ceramic has been to improve mechanical properties, there is a need to find a suitable compromise between different influences. In fact, adding carbon phases into ceramics usually leads to lower hardness. Its impact on fracture toughness is ambiguous, although certain mechanisms of increasing toughness are usually activated, such as crack deflection, crack branching and bridging, fiber and plate pull-out (Hvizdoš *et al.*, 2013a). Examples of initial work dealing with hot-pressed (2276K) SiC–CNT composites (Ma *et al.*, 1998) pointed to attractive trends when documenting a 10% increase in strength and fracture toughness of composites compared to a standard SiC prepared by the same method.

In the SiC based materials with the in-situ grown CNTs, their presence first led to a slight decrease of mechanical properties, but this decrease was insignificant. With further increase of CNT volume fraction, neither hardness nor fracture toughness did not decrease more (Fig. 9) (Džunda *et al.*, 2019).

Recent experiments with the addition of GNPs to the SiC ceramic sintered by conventional hot pressing show very promising trends. In this case, the addition of GNP was accompanied by increased porosity associated with them (and a corresponding decrease in hardness), but the fracture toughness values grew from 3 up to 4.5 MPa m^{1/2}, for GNPs of up to 6 wt%, Fig. 10(a). These results were also confirmed by K_{Ic} measured by the SEVNB method and also led to an increase in three-point bending

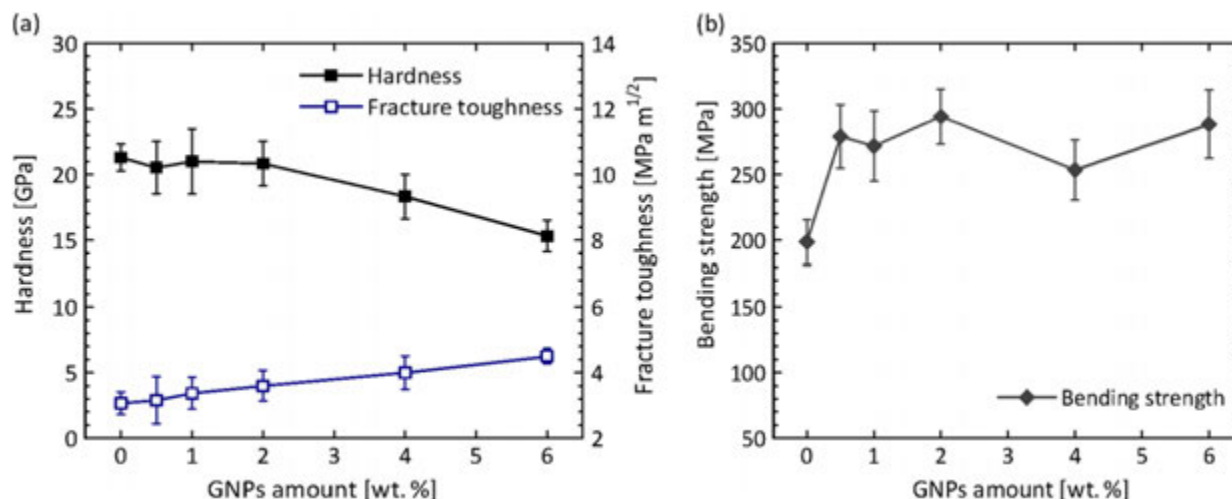


Fig. 10 Mechanical properties of SiC-GNP composites: (a) hardness and fracture toughness and (b) three-point bending strength. Reproduced from Hvizdoš, P., Fides, M., Kovalčíková, A., *et al.*, 2017. Electrically conductive SiC based composites – Development, microstructure, mechanical, electrical and tribological properties. In: Book of Abstracts of the Polish-Slovak-Chinese Seminar on Ceramics. Zakopane, Poland, pp. 74–75.

strength from 200 MPa for the reference sample to 260–300 MPa for the composites, **Fig. 10(b)** (Hvizdoš *et al.*, 2017). This behavior is due to activity of micromechanisms as described in other study (Hvizdoš *et al.*, 2013a). The action of GNPs is also well seen in the fracture surface as shown in **Fig. 4(a)**.

In the case of silicon nitride matrix ceramics, the present CNTs were accompanied by residual porosity and their mechanical properties were without exception lower than the reference samples. In addition to the problems with a good distribution, it turns out that it is also due to their strong tangling tendency and, paradoxically, relatively strong bonds to the matrix, which prevent their effective pull-out behind the crack tip and lead to their rupture (Hvizdoš *et al.*, 2011, 2012, 2013b). This behavior is typical and has been confirmed for CNTs prepared both ex-situ and in-situ (Gonzalez-Julian *et al.*, 2014) for different amounts of CNTs in Si_3N_4 .

In general, the Si_3N_4 matrix composites prepared by hot pressing (Balázi *et al.*, 2006; Hvizdoš *et al.*, 2012; Kvetková *et al.*, 2012; Hvizdoš *et al.*, 2013a; Balko *et al.*, 2014) had lower density (higher porosity) than the analogous monolithic material. Especially in the case of CNT additions, the reinforcement processes (e.g., grain and fiber pull-out, crack bridging, deflection and branching) were not sufficient to ultimately increase the global strength. This led to lower values of modulus of elasticity and fracture strength with increasing volume fraction of CNTs. However, by increasing the gas pressure and holding time for the composite with 1 wt% CNTs, it was possible to reach the same density as for the reference sample prepared at lower pressure (2 MPa). The modulus of elasticity decreased from the value for silicon nitride (approximately 250 GPa) linearly, with the measured density irrespective of gas pressure and for Si_3N_4 with 5 wt% CNT composite (with a density of about 2.2 g cm^{-3}) it was between 50 and 100 GPa. The relationship between the apparent density and three-point bending strength had a similar trend for these composites, i.e., a decrease in strength with an increase in CNTs volume fraction. In this case, however, the influence of pressure and sintering time was more pronounced and the materials prepared at higher pressures and times were considerably stronger.

Unlike CNTs, graphene nanoplatelets proved to be much better choice from the mechanical properties point of view. While the Si_3N_4 -GNP composites also experienced a decrease in hardness due to residual porosity, the fracture toughness increased significantly, **Fig. 11**. Kvetková *et al.* (2012) found that the addition of 1 wt% GNPs resulted in a K_{Ic} increase from $6.9 \text{ MPa m}^{1/2}$ for monolithic Si_3N_4 up to $7.84\text{--}9.92 \text{ MPa m}^{1/2}$ for composites made by simply admixing various types of commercially available GNPs. More detailed observations also revealed a detailed mechanism, where the presence of GNPs led to the crack growth hindering, that GNP pull-out can act far beyond the crack front and that the energy required to extract the graphene layer is higher than that of single- and multi-walled carbon nanotubes, due to the larger interfaces between GNP and matrix grains (Kvetková *et al.*, 2012).

In B_4C -GNP composites, hardness was governed by residual porosity and basically independent of the GNP content. In the HP and SPS materials, which were almost fully dense, the hardness was 20–24 GPa, while in the FS materials it was 15–17 GPa (Sedlák *et al.*, 2019). The fracture toughness, however, showed clear benefit of the GNP presence. It steadily increased from $3 \text{ MPa m}^{1/2}$ for B_4C up to $4.5 \text{ MPa m}^{1/2}$ for B_4C with 6 wt% GNP composite (Sedlák *et al.*, 2017). Here the typical platelets toughening mechanisms were clearly visible and demonstrated (Sedlák *et al.*, 2017).

Tribological Properties

Friction and wear represent the most important processes which occur on the interacting surfaces, in direct and indirect contact, and in relative motion. Generally, they can be analyzed as loss of energy (friction) and loss of material (wear) (Banjac *et al.*, 2014), and are a complex and complicated phenomenon that cannot be precisely predicted only by knowledge of other mechanical properties. So, wear

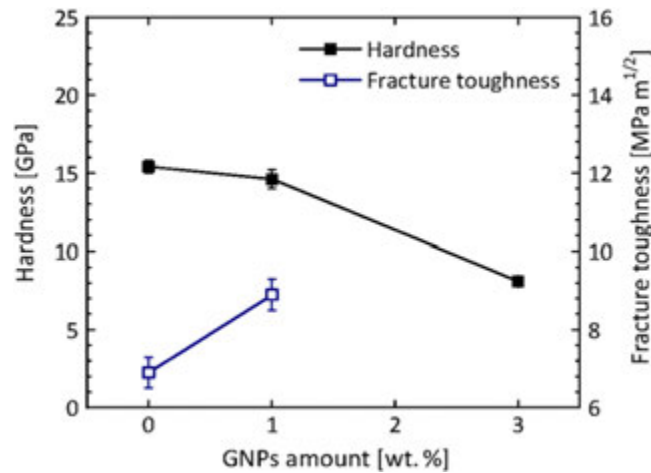


Fig. 11 Influence of the GNPs amount on hardness and fracture toughness of Si_3N_4 -GNP composites. (Kvetková *et al.*, 2012; Balko *et al.*, 2014).

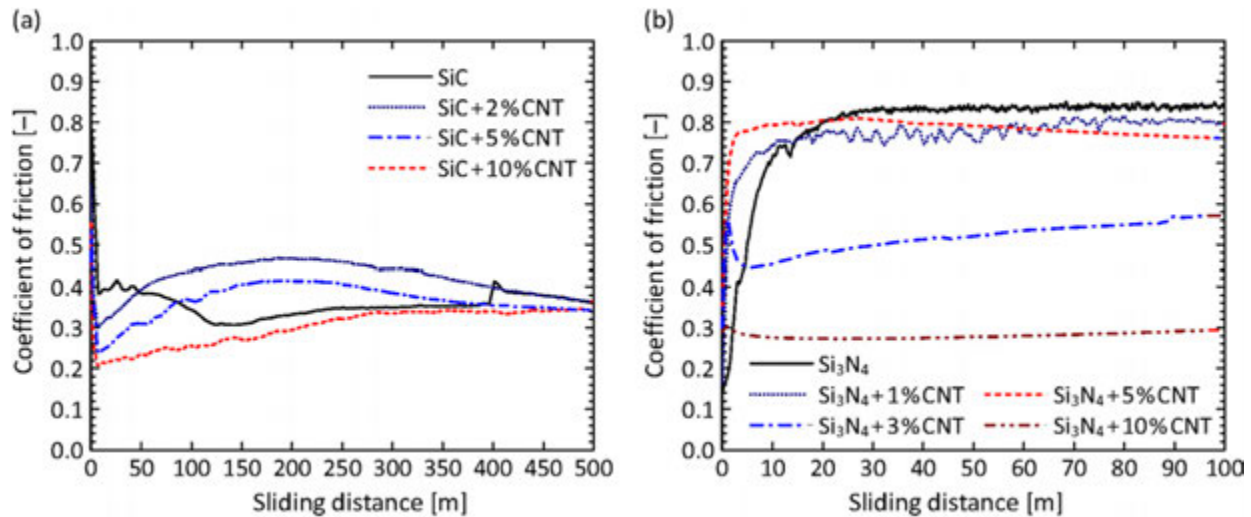


Fig. 12 Coefficient of friction during tribological tests at dry sliding conditions: (a) SiC-based composites with CNTs at 5 N load and 0.1 m s^{-1} sliding speed and (b) Si_3N_4 -based composites with CNTs at 1.5 N load and 0.1 m s^{-1} sliding speed. Reproduced from (a) Džunda, R., Fides, M., Hnatko, M., *et al.*, 2019. Mechanical, physical properties and tribological behavior of silicon carbide composites with addition of carbon nanotubes. *International Journal of Refractory Metals and Hard Materials* 81, 272–280. (b) Hvizdoš, P., Puchý, V., Duszová, A., Dusza, J., Balázs, C., 2012. Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. *Ceramics International* 38, 5669–5676.

tests are necessary in the development of new materials for tribological applications (Kato and Adachi, 2002). The fact is that tribological properties are the one that define possible application of material far more than their mechanical properties, since they are in better correlation with behavior in practice, regardless of the material type (Vencl *et al.*, 2008a,b, 2010, 2014; Kandeveva-Ivanova *et al.*, 2016; Vend, 2015a; Vencl *et al.*, 2015b). The wear of ceramic materials is usually characterized by its severity. In general, the wear regimes are divided into “mild” and “severe” (Adachi *et al.*, 1997; Kato and Adachi, 2002). For ceramics, this distinction is very well defined. Ceramics are considered to be useful in tribological components if their specific wear rate, i.e., W_s in Eq. (2), is less than $10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. The interval of 10^{-6} – $10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ is considered “transient”. At $W_s > 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, the wear is “severe”, which is usually connected to a change in damage mechanisms and means that the material is inadvisable to use.

Fig. 12 depicts examples of coefficient of friction (COF) profiles along the path of the wear tests (Džunda *et al.*, 2019; Hvizdoš *et al.*, 2012), similar to other experimental materials presented in other studies (Hvizdoš *et al.*, 2010, 2011). In all cases, after the short run-up phase (in order of meters), friction was relatively stable and reproducible. In some cases, a reduction in the coefficient of friction in composites can be observed, but, in general, small amounts of fillers in the form of nanoobjects, such as CNT and GNP, exhibit low efficiency in this respect. A relatively high amount ($> 10 \text{ wt}\%$) (Hvizdoš *et al.*, 2012) and relatively high loads ($> 50 \text{ N}$) (Belmonte *et al.*, 2013) are required for them to act as a solid lubricant.

The dependence of the coefficient of friction (COF) on the composition can be better observed in Fig. 13(a), which summarizes the average COF values for analyzed composites at low loads (5 N), and low sliding speed of 0.1 m s^{-1} . Silicon nitride ceramics

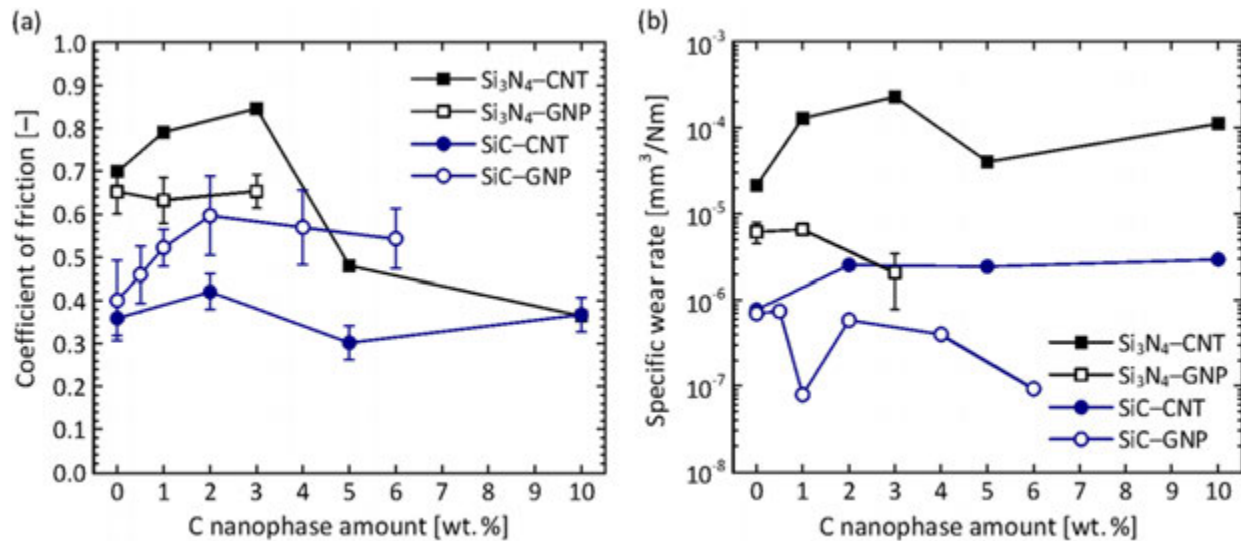


Fig. 13 Tribological properties as function of the amount of carbon (C) nanophases in the analyzed CMCs: (a) coefficient of friction and (b) specific wear rate (Hvizdoš *et al.*, 2011; Hvizdoš *et al.*, 2012; Hvizdoš *et al.*, 2017; Balko *et al.*, 2014; Džunda *et al.*, 2019).

generally exhibited higher friction than SiC-based composites. Particularly high levels were observed for the Si₃N₄ with low amount of CNTs. The coefficient of friction began to decrease when the CNTs amount reached about 5 wt%. In Si₃N₄ with 10 wt% CNTs, coefficient of friction values dropped to ~ 0.2 , making it interesting for applications such as dynamic seals or sliding bearings. In the case of the Si₃N₄ with GNP, the COF was essentially constant, although there were no higher carbon content materials available. The SiC-CNT composites exhibited very stable coefficient of friction (0.3–0.4), apparently related to the uniform distribution of the in-situ produced CNTs and to their strong anchoring within the SiC matrix (Džunda *et al.*, 2019). As a result, they could not be released in the contact zone and act as a solid lubricant. Very similarly, in SiC-GNP composites, COF even slightly increased with increasing carbon fraction (up to 0.6, at the highest C amount), apparently due to the coarse-grained structure and its higher porosity (again for the highest C amount).

Specific wear rates of analyzed composites at the same test conditions are shown in Fig. 13(b). In the SiC-based composites, the high-quality distribution and strong bonds of the in-situ produced CNTs on the SiC grains resulted in a very stable wear resistance of these materials. Similar behavior was also observed in the SiC-GNP composites, especially at low loads. Wear rate doubled only at loads of about 50 N (Hvizdoš *et al.*, 2016) and at high contents (6 wt%) GNPs. In general, however, the contribution of graphene has led to improved wear resistance.

Generally, the presence of CNT in the Si₃N₄-based composites leads to a reduction in wear resistance, especially due to imperfections and defects in the microstructure. However, some authors (Hvizdoš *et al.*, 2011, 2012) identified a certain optimum for about 5 wt% CNTs, where wear improved, most likely due to considerably reduced friction. At the higher amounts (10 wt% CNTs), the wear rate increased again to the values similar to those of Si₃N₄ with 1 wt% CNTs. Regarding the use of GNPs, in Si₃N₄ they seem beneficial in terms of wear behavior. As shown in Fig. 13(a), even at low amounts (1 and 3 wt% GNPs) there was no increase in coefficient of friction. Conversely, the wear rate decreased significantly (Fig. 13(b)), mainly due to improved fracture toughness (Hvizdoš *et al.*, 2013a). When testing Si₃N₄-GNP composites at elevated temperatures (300, 500 and 700°C), the positive effect of GNP was shown to be gradually diminishing, so that at 700°C the properties of the composites were comparable to those of reference ceramics (Balko *et al.*, 2014). On the other hand, it has been shown that, even at these temperatures, the GNPs remain structurally and chemically stable and do not decompose within the matrix (Balko *et al.*, 2014), Fig. 14(f). It was also found that the matrix material behaved stably under the used conditions. Only the β -Si₃N₄ phase was detected on both the surface and debris collected in the contact zone, as at the start of the tests. This means that no β -Si₃N₄ was transformed into α -Si₃N₄ (Balko *et al.*, 2014) during the testing at any stage.

In B₄C-based composites the coefficient of friction was similar in all materials (0.4–0.6), but wear rates showed benefit of the improved fracture toughness of GNPs containing composites. The wear was typically severe but W_s decreased from $1.5 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for monolithic B₄C by about 50% for B₄C with 6 wt% GNPs (Sedlák *et al.*, 2019).

Fig. 14 illustrates the typical damage at normal load of 5 N observed in wear tracks. Tests of monolithic Si₃N₄ left only a faint, quite smooth, polished tribological track, as shown in Fig. 14(d). For Si₃N₄-CNT composites more prominent surface abrasion with adhesion and more pronounced roughness of wear tracks was typical (Fig. 14(e)).

In the case of non-oxide ceramics, such as all SiC, Si₃N₄, and B₄C at higher loads and higher temperatures tribochemical reactions occur and oxide layers are formed on the wear track surface, most often in the form of SiO₂ islets (Balko *et al.*, 2014; Džunda *et al.*, 2019; Sedlák *et al.*, 2019), Fig. 14(a)–(c). Such oxidation and subsequent surface failure and microcracks formation were typical for both SiC-CNT and SiC-GNP composites (Fig. 14(a) and (b)). In our SiC-CNT composites, CNT agglomeration, so

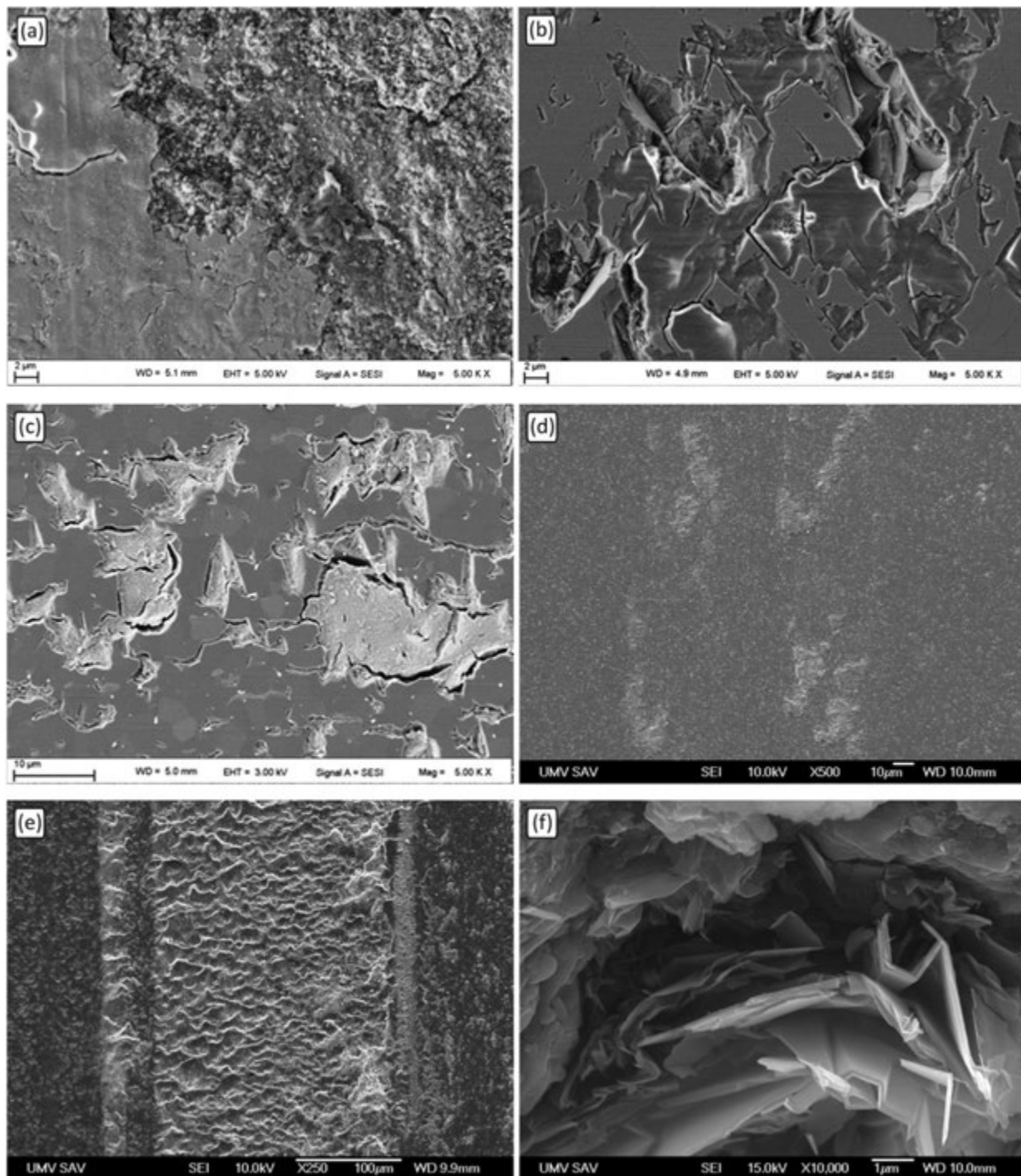


Fig. 14 Wear track damage of analyzed composites at normal load of 5 N: (a) SiC-CNT: formation and cracking of oxide tribofilm (SiO_2) in the contact zone, (b) SiC-GNP: microcracks, oxidation, (c) B_4C -GNP: GNP pull-out, exfoliation and creation of oxide tribofilm, (d) monolith Si_3N_4 : smooth, polished look, (e) Si_3N_4 -CNT: adhesive and abrasive wear and (f) Si_3N_4 -GNP: nanoplatelets agglomerate inside the wear track after the test at 500°C . Reproduced from (a) and (b) Hvizdoš, P., Fides, M., Kovalčíková, A., *et al.*, 2017. Electrically conductive SiC based composites – Development, microstructure, mechanical, electrical and tribological properties. In: Book of Abstracts of the Polish-Slovak-Chinese Seminar on Ceramics. Zakopane, Poland, pp. 74–75. (c) Sedlák, R., Fides, M., Hvizdoš, P., *et al.*, 2019. Boron carbide based ceramic composites prepared by SPS and flash sintering. In: Extended Abstracts of the 11th International Conference on the Science of Hard Materials (ICSHM11), pp. 155–156. Khao Lak, Thailand. (d) and (e) Hvizdoš, P., Puchý, V., Duszová, A., Dusza, J., Balázs, C., 2012. Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. *Ceramics International* 38, 5669–5676. (f) Balko, J., Hvizdoš, P., Dusza, J., Balázs, C., Gamcová, J., 2014. Wear damage of Si_3N_4 -graphene nanocomposites at room and elevated temperatures. *Journal of the European Ceramic Society* 34, 3309–3317.

often observed in conventional hot-pressed samples, was significantly suppressed and CNT distribution was relatively homogeneous. Thus, the efficient dispersion of CNT in the matrix has contributed to a better compaction of composites and to higher values of both mechanical and tribological properties.

In studies (Belmonte *et al.*, 2013; Gonzalez-Julian *et al.*, 2014; Miranzo *et al.*, 2017), the authors have shown that both the CNT and GNP, when randomly distributed, are beneficial only in relatively high amounts, i.e., 20% or more. Interesting results, however, have been achieved recently in the case of hierarchically grown graphene layers on alumina grains (Hussainova *et al.*, 2016). Here, an optimum with a reduced coefficient of friction and better wear resistance at a carbon content of only 1.5 wt% C or lower were found. The coefficient of friction was reduced from 0.65 to 0.5, while the wear rate decreased by 50%–60% in mild wear and up to 90% in severe wear regime.

Electrical Conductivity

The conductivity of multi-component composites consisting of conducting and non-conducting components is determined by the percolation phenomenon. In the vicinity of the percolation threshold of the conductive phase content in the non-conductive matrix, electrically connected conductive chains are formed and conductivity increases. At the critical limit of the conductive component content, there is a sharp increase in conductivity for a small increase in the content of this phase. It soon saturates and the further increase in the conductive component content only slightly affects conductivity (McLachlan *et al.*, 1990). In addition to the quantity, the particular nature of this transition also depends on the morphology and distribution of the conductive phase, and in particular on the interfaces at the impurity and matrix interface.

As shown in the section on microstructures, CNTs and graphene nanoplates are usually located along the grain boundaries of the matrix or in larger intergranular spaces. In the case of their interconnection, they can create linked networks. Such carbon phase networks, even though imperfectly interconnected, may be sufficiently electrically conductive due to the different mechanisms that include fluctuation-supported tunneling of charge carriers, or their jumping between individual carbon nanoparticles.

Inam *et al.* (2010) has collected and summarized a comprehensive series of work on electrical properties of various CMCs prepared by HP and SPS. It appears that about 5–10 wt% of carbon fiber structures are required to ensure percolation of the electric charge, the overall conductivity being in the order of tens to hundreds of S m^{-1} . The fine carbon black used as reference was generally less efficient, whereas the larger CNFs or larger amounts of SWCNT + MWCNT form the electrically conductive networks rather well (588 S m^{-1} for HP Al_2O_3 with 5 wt% CNF and 853 S m^{-1} for spinel (MgAl_2O_4) with 12.2 wt% CNT), respectively.

Similar results were found by others for various experimental materials based on zirconia, alumina, Si_3N_4 and SiC (Duszová *et al.*, 2008; Puchý *et al.*, 2011; Hvizdoš *et al.*, 2012; Džunda *et al.*, 2019). These are summarized in Fig. 15. It appears that in materials with CNTs the percolation threshold was in the range of 4–5 wt% C for Si_3N_4 , 2–3 wt% C for Al_2O_3 and around 1 wt% C for ZrO_2 . The slower increase in conductivity of Si_3N_4 ceramics appears to be due to imperfections in the microstructure – residual porosity and CNTs agglomeration. In alumina composites, the electrical conductivity increased from zero to a maximum of 140 S m^{-1} at 10 wt% CNTs. An analogous material prepared in the same way, but with the addition of carbon black, exhibited an electrical conductivity of about one order of magnitude lower, e.g., for 5 wt% C, the conductivity was $90.5 \pm 4.8 \text{ S m}^{-1}$ for the CNTs but $8.5 \pm 0.1 \text{ S m}^{-1}$ for the carbon black (CB). That is, the carbon black random morphology resulted in a limited linking of the graphite particles so that the conductivity was substantially lower, confirming the advantage of using the 1D particles.

For the nanocarbon-doped SiC materials, the percolation threshold was about 1–2 wt% C (Fig. 15(b)) and for CNT at 5 wt% conductivity was sufficient ($> 1000 \text{ S m}^{-1}$) for practical use of EDM to machine such composites – in particular 1448 S m^{-1} for SiC with approx. 5 wt% CNTs and 2873 S m^{-1} for SiC with approx. 10 wt% CNTs. However, in the case GNP, the further increase was lower and conductivity remained below 1000 S m^{-1} , which was probably due to difficulties in achieving their truly homogeneous distribution and the formation of sufficiently dense conductive networks. Similarly, in B_4C –GNP the conductivity only for higher amounts (8 wt%) of GNPs reached over 1000 S m^{-1} , and even then only in a specific direction (Sedlák *et al.*, 2017).

In the recent literature (Drozdova *et al.*, 2016; Hussainova *et al.*, 2017), it was reported that through the hierarchical structure forming, when the graphene layers are grown in-situ on grain surfaces of a non-conductive matrix (alumina, zirconia), the percolation threshold was reached already at a carbon content of 0.2 wt%, by a scalable and potentially industrially useful manufacturing methods. This confirms the practical possibility of the tailored structure building to achieve the desired properties of advanced ceramic composites.

Based on these results, due to its fibrous or lamellar (1D, 2D) structure, it can be concluded that a very small amount of carbon is sufficient to reliable percolation of the electric charge (only 1–5 wt%, but potentially even less, depending on the microstructure of the matrix). In this way, in some CMCs it is possible to increase electrical conductivity of up to 13 orders of magnitude.

Conclusions

In order to improve the applicability and ease of machining of hard-to-machine CMCs with the SiC, Si_3N_4 , and B_4C matrices without seriously compromising their other excellent properties, new composites have been developed. The addition of modern “low-dimensional” (1D – nanotubes and 2D – nanoplatelets) carbon nanophases was used. The materials thus prepared were examined for microstructure, mechanical, tribological and other functional properties.

The introduction of carbon 1D (nanotube) and 2D (nanoplatelet) fillers usually leads to a finer microstructure. It is also associated with residual porosity and almost inevitably leads to a decrease in hardness. Only in B_4C , where carbon acts as sintering

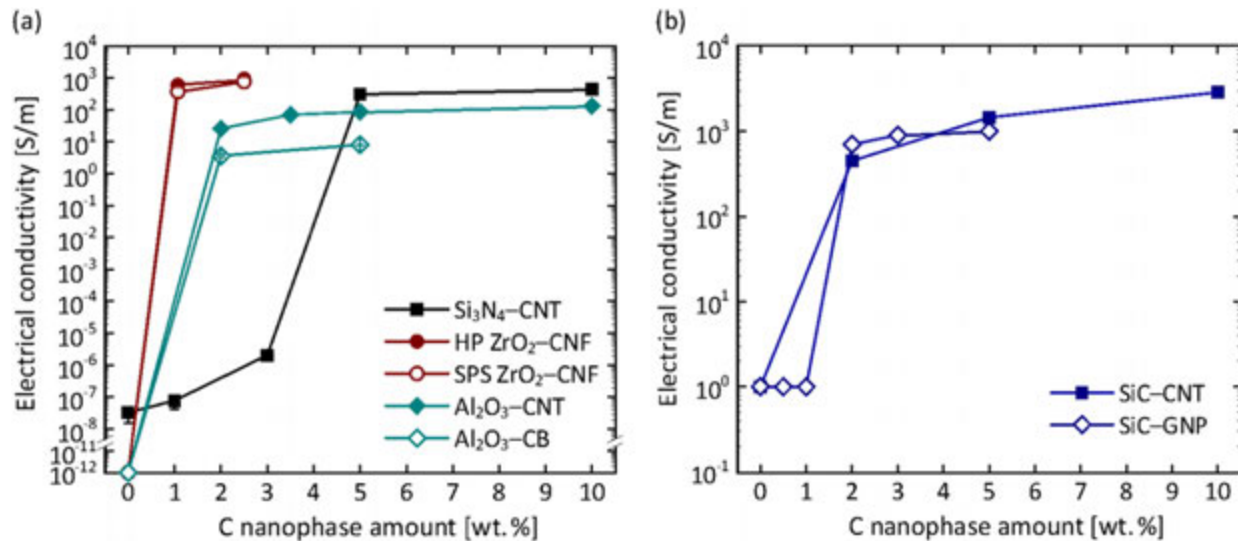


Fig. 15 Electrical conductivity as function of the amount of carbon (C) nanophases in and percolation thresholds in various CMC with carbon nanophases: (a) Si₃N₄ and other non-conductors and (b) SiC (Hvizdoš *et al.*, 2017; Džunda *et al.*, 2019). (a) Reproduced from Hvizdoš, P., Puchý, V., Duszová, A., Dusza, J., Baláži, C., 2012. Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. *Ceramics International* 38, 5669–5676.

promoting additive, its presence actually improved the densification. In terms of fracture toughness, the results have so far been ambiguous, especially in the case of higher proportions of carbon nanophases. In any case, however, the potential for increased toughness is clearly demonstrated through active micro-toughening mechanisms, such as fiber and plate pull-out, crack growth inhibition through bridging, branching, or deflection. In this respect, further fillers are needed to optimize the interface between the ceramic matrix grains and the carbon nanophases, which will provide sufficient bond strength but at the same time allow the activity of the mentioned mechanisms.

Tribological tests have shown that the CNTs and GNPs generally led to a reduction in the coefficient of friction only in some specific cases at higher CNTs amounts, i.e., above 5 wt%. In the case of CNT containing composites, there is generally a slight decreasing tendency in wear resistance, but in some cases an optimum has been identified (e.g., for Si₃N₄ with 5 wt% CNT), where the wear rate was the same as for the monolithic material at a much lower coefficient of friction. In the case of GNPs, if they are uniformly distributed in the matrix, there is a clear benefit in improving wear resistance due to improved fracture toughness (notably in B₄C-GNP composites). The coefficient of friction in these composites usually does not change greatly and remains stable during the tests. Wear rate can be significantly reduced in some cases (up to 60% for Si₃N₄ with 3 wt% GNP). Very good stability of GNP and Si₃N₄ grains up to 700°C was also shown.

The electrical conductivity can be significantly increased and already small amounts of CNT or GNP are sufficient to convert the electrical insulator into a functionalized conductive ceramics. A uniform distribution here also proves to be critical, particularly in the case of graphene nanoplatelets, since it is very complicated to prepare sufficiently interconnected conductive networks by conventional powder mixing techniques. At the same time, there has been identified a positive trend, where by designing of tailored hierarchical structures very low amounts of carbon can ensure optimal electrical properties.

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Polymer-Ceramic Nanocomposites and Converging Technologies

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Nomenclature

0-D nanocomposites Zero dimensional nanocomposites
1-D nanocomposites One dimensional nanocomposites
2-D nanocomposites Two dimensional nanocomposites
3-D nanocomposites Three dimensional nanocomposites
BaTiO₃ Barium titanate
CNTs Carbon nanotubes
CO₂ Carbon dioxide
f-G Functionalized graphene
GPa Gigapascal
IoT Internet of Things
IPN Interpenetrated networks
LED Light emitting diode
MEMS Micro-electro-mechanical systems
MOFs Metal-organic frameworks
MWCNTs Multi-walled carbon nanotubes
NC Nanocrystalline cellulose

NEMS Nano-electro-mechanical systems
nm Nanometer
PANI Polyacrylonitrile
PbTiO₃ Lead titanate
PEO Polyethylene oxide
PET Polyethylene terephthalate
PHAs Polyhydroxyalkanoates
PMMA Polymethyl methacrylate
PVDF Polyvinylidene fluoride
PVDF-TrFE Polyvinylidene fluoride – trifluorethylene
PZT Lead zirconate titanate
SiC Silicon carbide
SiO₂ Silicon dioxide
TiO₂ Titanium dioxide
UPe Unsaturated polyester
wt% Weight percent
ZnO Zinc oxide

Glossary

Actuator It is a device that converts some type of stored energy into mechanical energy, thereby generating mechanical force and providing controlled movements or positioning. According to the input signal, an actuator can be operated electrically, by fluids (pneumatic and hydraulic actuators), or by thermal or mechanical means, etc. Actuators have become known as the "muscle" of the mechatronic systems, as they create linear and rotary motion, or a combination of these types of motion. They are increasingly driven and controlled by software.

Carbon nanotubes (CNTs) CNTs are cylindrical molecules that occur in the form of a rolled-up single sheet of graphene (single-walled CNTs – SWCNTs, with a diameter less than 1 nm), or in the form of rolled-up multiple sheets of graphene. In the latter case, CNTs consist of several concentric interlinked cylinders of sp²-carbon atoms and are called multi-walled CNTs (MWCNTs). Due to their nanostructure and the strength of the bonds between atoms, CNTs provide development of ultra-high strength and low-weight materials, that possess high electrical and thermal conductivity.

Delay line It is an electrical or optical component that makes it possible to control the time delay of a signal. The introduction of a calculated delay is necessary for the proper functioning of some systems, as the input signals are often transmitted much more quickly than systems can handle and interpret it. Delay lines are especially important for communications and signal processing. Electrical delay lines can generate time delays ranging from a few nanoseconds to several microseconds. An optical delay line has a much wider bandwidth and a higher speed. Delay lines might be analog or digital.

Magnetostriction It is a property of ferromagnetic materials. The term is related to the change in dimensions (stretch or shrink) of a ferromagnetic sample, due to the magnetization occurring when material is subjected to a magnetic field. Variations in the applied magnetic field are accompanied with the variation of the degree of magnetization in the material, leading to a change in the magnetostrictive strain, until reaching the magnetization saturation value. On the other hand, when a mechanical force is applied to these materials – the materials induce a magnetic field. This field can be used to create an electric current, thus transforming mechanical energy into electrical energy.

Mechanical activation It is an activation process based on the application of mechanical shock and stress to the treated system, whereby a series of physical and chemical effects, in terms of structure changes, is initiated. One of the most common procedures for such an activation is the processing of materials in the so-called triboreactors (such as attritors, vibratory mills, planetary mills, and other high-energy mills).
MEMS/NEMS MEMS/NEMS are systems of miniaturized mechanical and electro-mechanical elements (devices and structures) that are made using micro- or nanofabrication techniques. The critical physical dimensions of MEMS and NEMS devices can range from below one micron to several millimeters and from 1 to 100 nm, respectively. Although MEMS devices are primarily complex electromechanical systems with multiple moving elements under the control of integrated microelectronics, they can still consist of relatively simple structures with no moving elements. However, the minimal criteria that should be met include the presence of elements that have some sort of mechanical functionality, even if they cannot explicitly move. This

system usually consists of a central unit that processes data (the microprocessor) and several components that interact with the environment. The most important functional elements of MEMS are microsensors and microactuators. MEMS are also known as micromachines or micro systems technology. In the case of NEMS, where the physical motion of a nanoscale structure is relevant, the appearance of quantum effects is also important.

Perovskite It is a common name for a group of materials with the chemical formula ABO_3 , with a crystal structure which is the same (cubic) as that of mineral calcium titanate. Perovskites often display a number of interesting properties, including superconductivity, giant magnetoresistance, and ferroelectricity. Recently, their application in providing clean energy has drawn significant scientific attention, primarily in the development of perovskite solar cells.

Thermistor It is a type of electrical resistor, the resistance of which greatly depends on temperature. There are two types of thermistors: Positive Temperature Coefficient (PTC) thermistors and Negative Temperature Coefficient (NTC) thermistors. When the temperature increases, the resistance of a PTC thermistor will increase as well, while the resistance of a NTC thermistor will decrease.

Transducer It is a device that transforms one form of energy into another. Therefore, one type of signal (one type

of physical quantity) can be converted into another. The input signal, as well as the resulting signal can be of any useful physical form (mechanical, optical, thermal, chemical, electric, etc.). The devices that offer an electric output are called sensors.

Wave filter It is a device used to separate waves based on the difference in frequency. This device is an important part of signal processing, since it can remove unwanted components or features from a signal. Electric wave filters transmit certain bands of frequencies and attenuate the rest, enabling the separation of a broad-frequency band into narrow bands, in any desired manner. Although electronic filters were originally entirely passive (consisting of resistance, inductance, and capacitance), active technology (relying in the utilization of transistors or op-amps in addition to resistors and capacitors) provide gain and frequency adjustment flexibility and pose no loading problem due to a high input impedance and a low output impedance. They are also less expensive, easier to designing and they open up new possibilities in filter specifications. Among acoustic wave filters, which are electromechanical devices, surface acoustic wave (SAW) filters and bulk acoustic wave (BAW) filters are competing for their shares in new technologies.

Introduction

A growing interest in converging technologies in scientific, technological and policy circles is a result of an increased demand for developing a future generation of devices, network technologies, connected smart objects interfaces and other evolving innovations. Advances in these technologies have the potential to provide solutions to numerous societal challenges, such as advanced healthcare, environmental remediation, sustainable development, and adoption of cyber-physical systems based on the Internet of Things and the Internet of Systems. The term 'converging technologies' is frequently used for groups of technologies, such as nano-, bio-, and information technologies, with potential links between them and resultant synergies and benefits. There is a common agreement that the convergence of these diverse technologies is based on the understanding of complex hierarchical structures and systems, as well as on the material unity at the nanoscale and on technology integration from that scale (Roco and Bainbridge, 2003).

The interest in nanostructures and their application in various electronic devices, biosensors, solar cells and nanodevices is related to their unique properties at the nanoscale, where the performance of materials can change dramatically. The increased need for multifunctional materials with improved properties, such as high strength performance, good thermal, mechanical and physical properties, gas barrier, transparency and safety, has induced the development of various types of nanocomposites. In these materials, which can be classified as metal matrix composites, ceramic matrix composites and polymer matrix composites, at least one of the chemically and physically different phases within the system is smaller than 100 nm. Among them, polymer-ceramic nanocomposites are especially important due to their outstanding mechanical properties, barrier resistance, flame retardancy, electrical, magnetic and optical properties, easy formability, small weight, and low cost.

Polymer-Ceramic Nanocomposites Structure and Classification

The development of polymer-ceramic nanocomposites is closely linked with the optimization and modification of synthesis routes and the study of the mechanisms that control their structure and properties. Their properties do not depend only on the properties of individual components and on the process used in nanocomposite fabrication, but also on the degree of the mixing between the matrix and the reinforcement material, the nature of the interphase and the type of adhesion at the matrix interface, as well as on the type, size, and shape of the reinforcement nanomaterial and the morphology of the system.

The internal structure of all composites consists of: (1) a matrix phase, which is continuous, (2) a reinforcement material, which is scattered and surrounded by the matrix, and (3) the interface between the reinforcement phase and the matrix phase.

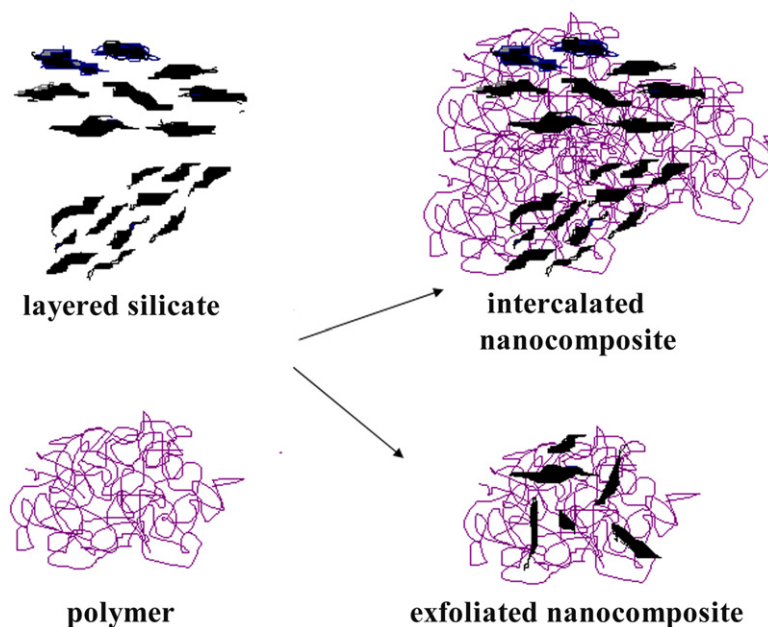


Fig. 1 Structure of intercalated and exfoliated nanocomposites.

Polymer-ceramic nanocomposites are the materials that have a polymer as a matrix material, while various ceramic nanomaterials can be used as a reinforcement material. According to the state of the composite in its functional form, these materials can be: solids, quasi-solids (gels), and liquids (composite solutions).

The polymer matrix plays an important role in determining the processability, mechanical properties, heat resistance and the resistance to environmental media of polymer-ceramic nanocomposites. The main purpose of the matrix is to bind the reinforcement phases in place and to distribute stress among the constituent reinforcement materials under an applied force. The most commonly used types of polymers for the matrix phase are thermosets, thermoplastics, and elastomers. While thermosets, such as polypropylene, polystyrene, polyethylene, polycarbonate, nylons, and polyacetals, have cross-linked or network structures with covalent bonds with all molecules, thermoplastics (polyesters, silicone, phenolics, epoxies, ureas, melamine, and polyimides) consist of linear or branched chain molecules with strong intramolecular and weak intermolecular bonds. Elastomers, such as natural rubber, chloroprene rubber, butyl rubber, ethylene propylene rubber, synthetic polyisoprene, polybutadiene, and fluoroelastomers, can be stretched easily, but they can also return to their original shapes when the force or stress is removed, due to their loosely cross-linked polymer structure.

Nanocomposites differ from conventional composites due to an exceptionally high volume-to-surface ratio of the reinforcing nanomaterials. Nanoscale morphologies of the reinforcing material can consist of nanoparticles, nanofibers, nanotubes, or lamellar nanostructures. Although there are many classifications of nanocomposites (according to synthesis routes used for their fabrication, fields of application, type of used polymer matrix, etc.), one of the most common classifications of these materials is based on the dimensional morphology of the reinforcing ceramic nanomaterial. In this context, polymer-ceramic nanocomposites can be classified as: zero dimensional nanocomposites (0-D nanocomposites), one-dimensional nanocomposites (1-D nanocomposites), two-dimensional nanocomposites (2-D nanocomposites) and three-dimensional nanocomposites (3-D nanocomposites) (Salavati-Niasari and Ghanbari, 2011). According to another classification of polymer-ceramic nanocomposites, based on the structure of the reinforcing material, they may be divided into: particulate nanocomposites, fibrous nanocomposites, and layered nanocomposites. Furthermore, particulate composites can be classified as composites with random particle orientation and composites with preferred particle orientation, while fibrous composites can be classified as short-fiber reinforced composites with random or preferred fiber orientation and long-fiber reinforced composites with unidirectional or bidirectional fiber orientation.

Depending upon the degree of the dispersion of nanosized layered structure, polymer-ceramic nanocomposites can be divided into intercalated and exfoliated nanocomposites (Fig. 1). In intercalated nanocomposites, the polymer alternates with the inorganic layers in a fixed composition ratio, while in exfoliated nanocomposites, the polymer chains between the layers are almost continuously variable. Furthermore, the exfoliated nanocomposites can be subdivided into ordered and disordered exfoliations, while the term partial exfoliation is used to describe an intermediate morphology between intercalation and exfoliation.

An important part of every polymer-ceramic nanocomposite is the interface between the matrix and ceramic nanoreinforcement. It is well established that the properties, composition, and microstructure vary across the interface region, which is different from both matrix and reinforcement. The area of the interface between the matrix and nanoreinforcement is typically an order of magnitude higher than the conventional composites. If the interface region has a good interaction between the polymer chains of

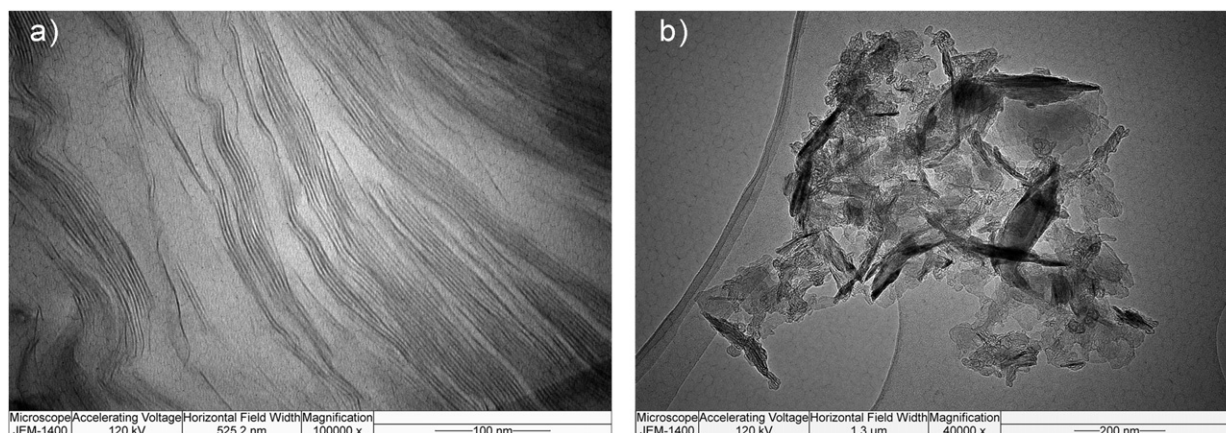


Fig. 2 Microstructure of polymer-clay nanocomposites.

the matrix phase and the surface of the reinforcing nanomaterials, the overall properties of the nanocomposite will be improved. In terms of interactions between components, polymer composites can be classified as natural composites, chemical composites and physicochemical composites or interpenetrated networks (IPN). In natural composites (interpolymeric complex), ionic, hydrogen, and van der Waals bonds occur between components, while chemical composites are characterized by covalent bonds established between compounds. For physicochemical composites, the chains of one component (cross-linked or not, by covalent bonds) are "fixed" in the reticular structure of the second component (Florea and Carcea, 2012).

The Applications of Polymer-Ceramic Nanocomposites

The application of polymer-ceramic nanocomposites in various electronic and optoelectronic devices, biosensors, solar cells, smart food packaging, biomedical devices, and bone-bioerodible materials for skeletal tissue repair, has increased tremendously over the past several years. In the context of converging technologies, the main applications of polymer-ceramic nanocomposites include electronic and energy conversion, biotechnology and medicine, as well as environmental protection and remediation. Improvements in thermal and mechanical properties of polymer nanocomposites have also resulted in some more general/industrial applications, ranging from transportation and safety to construction and coating industries. Examples of such materials include segmented copolymers, which combine polyurethane and polysiloxane block structures and various other composites that combine different organic and inorganic materials. In order to improve the thermal, mechanical, surface, and barrier properties of polyurethane-based nanocomposites, low quantities of clay nanofillers can be inserted into the polymer matrix (Fig. 2) (Stefanović *et al.*, 2017). Over the past several years, the montmorillonite clay/polymer nanocomposites filled with low loadings (< 5 wt%) of clay have attracted huge interest by the anticorrosion coating industry, thanks to the significantly enhanced corrosion stability (Tomić *et al.*, 2018). The favorable properties of these materials largely depend on a better interfacial interaction between polymer and ceramic nanomaterials with a higher surface area.

High strength, low permeability, and excellent flame-retardant properties make nanoclays an affordable nanofiller, suitable for the development of numerous other nanocomposites, used in transport industries. Besides nanoclay, various other nanofillers such as alumina, carbon nanotubes, nanocarbon, TiO₂, SiC, and PZT can be used for the development of polymer-ceramic nanocomposites suitable for application in the field of aerospace industries.

Polymer-Ceramic Nanocomposites for Electronics and Energy Conversion Applications

Polymer-ceramic nanocomposites for electronic and energy conversion applications are known as smart polymer-ceramic composites. Smart materials are materials with built-in sensing and/or actuation functions. These materials respond to external stimuli (pressure, electrical or magnetic field, heat, light, chemical stimuli or nuclear radiation), undergoing the change of one or more properties. The term 'smart' describes self-adaptability, self-sensing, memory, and multiple functionalities of the materials or structures. Smart polymer-ceramic nanocomposites are closely related to the design of advanced devices for electronic and optoelectronic applications. The high technological interest in this kind of nanocomposites in the context of electro-optical applications lies in their potential application for the production of LEDs, laser diodes, and photovoltaic devices. All these devices rely on the light-matter interaction and the electronic properties of matter, while converting light into electrical signal or vice versa. In this field, semiconductor ceramic nanoparticles/polymer nanocomposites are identified as promising materials, since it is expected that their optical properties will be determined by the quantum confinement size effect of the semiconductor. It has been demonstrated that, depending on the particle size, shape, and the surrounding dielectric matrix, ceramic nanoparticles can exhibit characteristic plasmon resonance modes during interaction with electromagnetic waves, as a result of collective oscillations of free

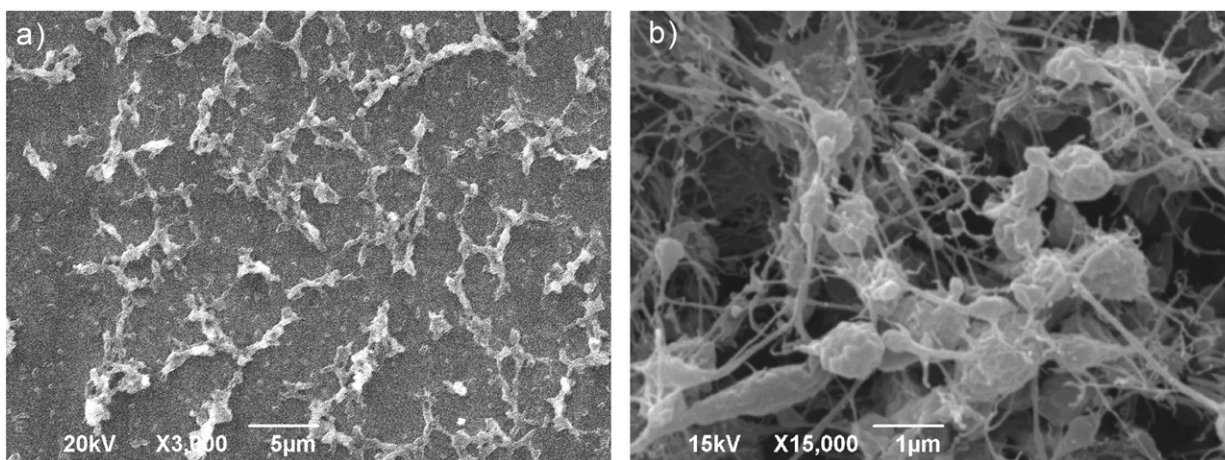


Fig. 3 PVDF-ceramic nanocomposites in the form of: (a) thin films, (b) nanofibres.

electrons and the local enhancement of the electromagnetic field. Beside the high temperature resistance and processability, other general requirements for these materials include transparency (which is especially required for devices operating in the near-infrared region), particle morphology and distribution control, as well as the ability to tune the band edge and particle size of the used nanoreinforcement.

Another interesting application area of smart polymer matrix nanocomposites is certainly the Internet of Things (IoT), since this concept requires miniaturized, low-power microelectronic systems based on micro controllers, transceivers, sensors, and energy supply (Vermesan and Friess, 2013). Internet of things is a concept involving a system of interconnected computing devices, machines and everyday physical objects provided with unique identifiers and able to communicate with other devices by transmitting data through a network, without requiring direct human-to-human or human-to-computer interaction. Materials used for devices in IoT exhibit a wide range of physical (piezoelectric, magnetostrictive) and chemical (catalytic, electrochemical and chemical sensing) properties, which can adapt and/or respond to their environments (Gibson, 2010). Typical applications of these materials include ultrasonic transducers, actuators, resonators, wave filters, delay lines, transformers, pressure sensing devices, energy harvesting devices, etc. (Petrović *et al.*, 2018).

The application of these materials in various miniaturized mechanical and electro-mechanical elements, such as piezoelectric micro- and nano-actuators and sensors in micro- and nano-electro-mechanical systems (MEMS/NEMS devices and structures), ranges over many technological fields from aerospace, military and industrial, to instrumentation and medical applications. The incorporation of nanocrystalline particles into easily processable polymer matrices allows the modification of polymer-ceramic nanocomposite physical properties and the implementation of new features in the polymer matrix. These materials can be fabricated in numerous forms, including thick and thin films, as well as various nanofibre composite structures (Fig. 3).

It has been observed that the host polymers influence the spatial arrangement of the ceramic nanoparticles during the in situ synthesis. Additionally, it has been shown that the geometry of the filler particles plays an important role in tailoring the material's properties. Furthermore, a high surface-to-bulk ratio of ceramic nanoparticles may significantly affect the matrix, leading to some new properties that are not present in either of the pure materials. In a diphasic piezocomposite, there are ten different possibilities regarding the orientation of the material in 3D space (Fig. 4). The so-called 0–3 piezocomposites (in which piezoelectric ceramic particles are homogeneously distributed within the polymer matrix) have been proven to be especially useful, since they can take various shapes, while remaining piezoelectrically active. On the other hand, in order to synthesize smart polymer nanocomposite materials with more sophisticated features, it is necessary to start with nanomaterials with well-defined and controlled specific properties, such as morphology, chemical composition and defect structure, surface functionalization, etc.

When ferroelectric ceramic nanoparticles are used as fillers for piezo-nanocomposites, two significant factors affect their physical properties. One is the macroscopic effect related to the surface tension of the nanoparticle, while the other is related to the grain size effect on microscopic interactions which induce ferroelectric instability. It has been reported that in perovskite oxides, spontaneous polarization decreases with particle size reduction, eventually disappearing if the conditions for the size-driven phase transition are fulfilled. The critical grain size in ferroelectrics has been defined as the one at which the ferroelectric–paraelectric (e.g., tetragonal–cubic) phase transition takes place. The majority of literature data indicate that the critical crystallite size generally depends on the powder preparation method. Although in some cases it is close to 100 nm, it has been shown that mechanical activation can lead to the formation of nanocrystalline powder with a tetragonal ferroelectric structure even for particles as small as ~30 nm (Pavlović *et al.*, 2007). The preservation of the ferroelectric crystal structure in the particles with sizes reduced to the nano-range is especially important having in mind the general requirements in the miniaturization of ferroelectric components, as well as the ability of nanoparticles to facilitate the occurrence of certain crystal phases of the polymer within the polymer composite.

Numerous researchers have pointed out that the particle size and the surface-to-volume aspect ratio of the ceramic filler, together with the amount of the filler, influence interfacial distances in the composite. Namely, the polymer matrix often interacts

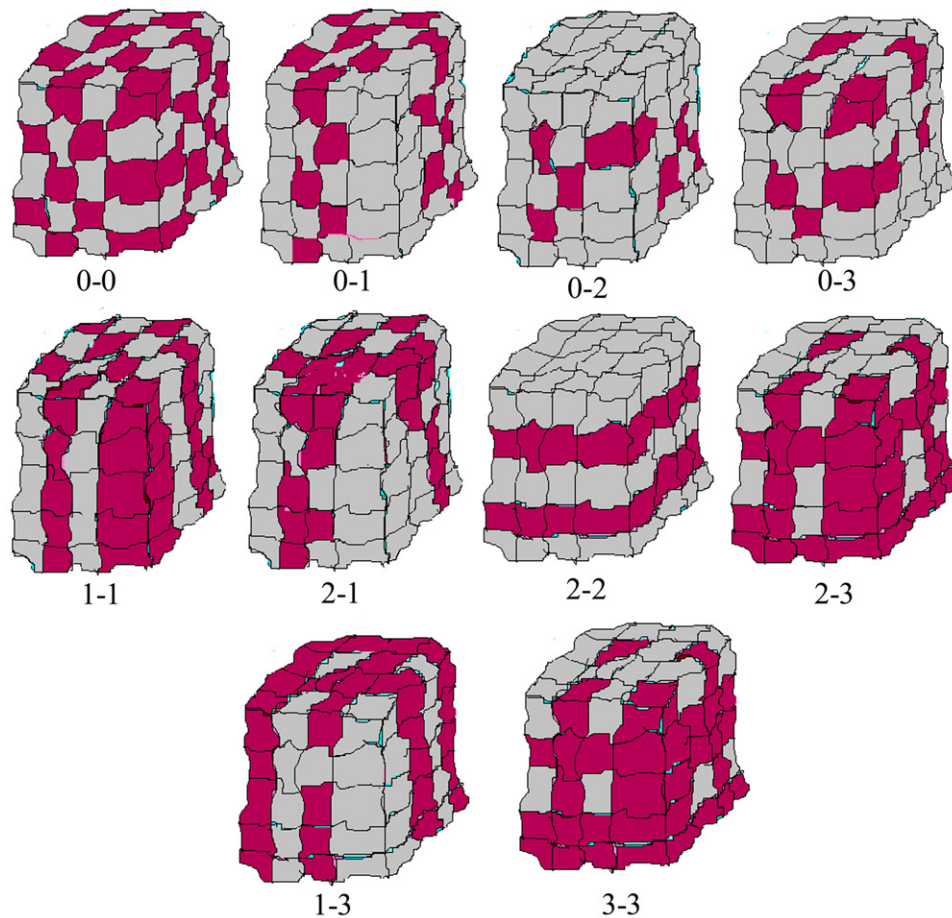


Fig. 4 Connectivity patterns for diphasic composites (the first index denotes the connectivity of the ceramic filler, while the second index designates the connectivity of the polymer matrix).

better with ceramic particles that are smaller in size and/or have higher surface-to-volume aspect ratios. The filler particle size reduction is also followed by a decrease in the inter-particle distances, which can trigger the far-field effect between neighboring nanoparticles, thus changing the dielectric permittivity of the material. Ceramic fillers with high surface-to-volume ratio also tend to self-assemble into skeleton-like superstructures, thereby affecting dielectric losses. Usually, a high concentration of the ceramic filler is necessary to increase the permittivity of the composite. On the other hand, a higher number of defects and percolation effects related to the increase of the filler particle concentration may cause a significant drop in dielectric strength.

Mechanical activation has been confirmed as an effective method for the modification of the physico-chemical properties of multifunctional ceramic nanoparticles, which can be used as nanoreinforcement in various forms of piezopolymer-ceramic nanocomposites (**Fig. 5**). The introduction of mechanically activated ceramics into a polymer matrix, e.g., into polyvinylidene fluoride (PVDF), predominantly induces the crystallization of the highly desirable electrically active semicrystalline phase of PVDF, making these composites suitable for application in the next-generation electronic devices (*Pavlović et al., 2013; Peleš et al., 2018*). The changes in the morphology of these materials have shown that the reduced sizes of the filler do affect not only the crystallization of the PVDF, but also the mechanical and dielectric properties of polymer-ceramic nanocomposites, such as PVDF/PMMA-BaTiO₃ (*Mofokeng et al., 2014*). It has been found that the utilization of BaTiO₃ as a nanofiller can increase recoverable energy densities in epoxy-based nanocomposites for electrical energy storage, while BaTiO₃-PMMA nanocomposites with a well-defined core-shell structure exhibit a high dielectric constant and low inherent losses, in a wide range of frequencies and temperatures (*Xie et al., 2011*).

Other nanoceramic materials can also be used as fillers for multifunctional piezoelectric nanocomposite production. Polyvinylidene fluoride-trifluorethylene (PVDF-TrFE) and PZT composites have been prepared by solvent casting and subsequent compression molding and investigated with respect to their piezoelectric and pyroelectric behavior (*Ploss et al., 2001*). It has been observed that the resulting pyroelectric and piezoelectric coefficients cannot be derived from the simple mixing rule applied to the matrix and the active filler. Theoretical calculations indicate the important impact of the piezoelectric anisotropy of the PbTiO₃ active filler on the characteristics of the resulting composite (*Glushanin et al., 2006*). In order to achieve a better interfacial interaction, graphene oxide-coated silica nanoparticles have recently been fabricated by electrostatic assembly, to be subsequently

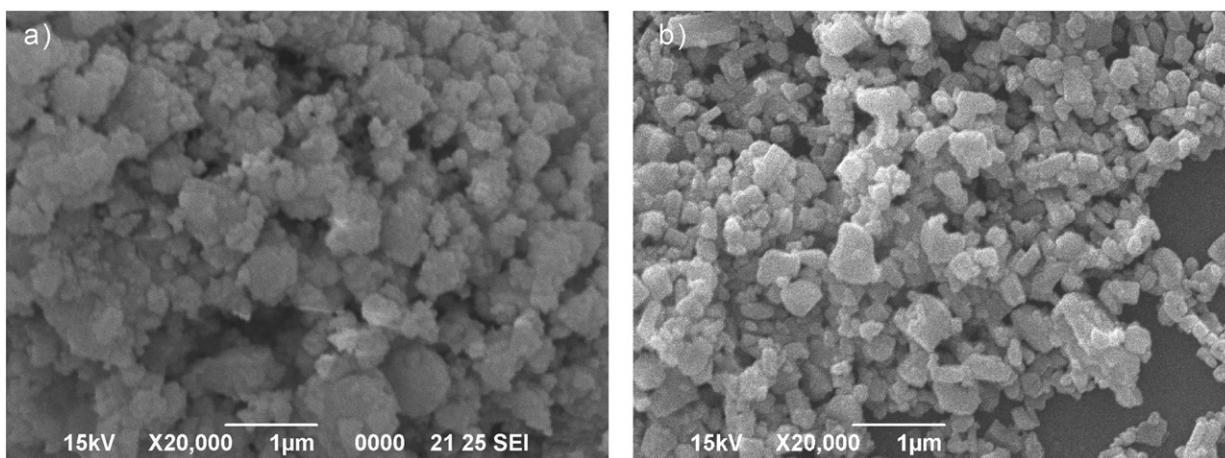


Fig. 5 SEM micrographs of the mechanically activated reinforcement: (a) BaTiO₃, (b) ZnO.

blended with PVDF. A novel nanocomposite for efficient strain sensing, exploiting a combination of functionalized graphene (f-G) and PVDF has been investigated, as well (Eswaraiah *et al.*, 2011).

Another important application of polymer-ceramic nanocomposites is in the production of energy harvesting devices. These devices ensure the collecting and storing of a certain amount of ambient energy (energy from external sources, such as solar energy, thermal energy or energy from the radio-frequency signals, flow-based and vibration energy, etc.), in order to provide power for wireless autonomous devices, thereby offering a good alternative to primary (non-rechargeable) batteries. The utilization of those devices relies on the application of photovoltaic cells, thermoelectric and pyroelectric transducers, converters of radio waves to direct current, etc. Energy harvesting applications such as nanogenerators, nanoscale materials and various potential devices based on PVDF have been developing rapidly due to the material's piezoelectric and pyroelectric properties. This includes the conversion of mechanical vibrations into electrical energy via piezoelectric effect and the conversion of thermal fluctuations into electrical energy by pyroelectric effect. Furthermore, hybrid systems for energy harvesting are possible to achieve since piezoelectric and pyroelectric effects are always present simultaneously (Ruan *et al.*, 2018; Kim *et al.*, 2011; Gusarov *et al.*, 2016).

Beside ferroelectric fluoropolymers (PVDF and its copolymers), other polymers, such as polyethylene oxide (PEO), polyacrylonitrile (PANI) and polymethyl methacrylate (PMMA), are used as polymer nanocomposite matrices in various energy storage devices, especially as polymer electrolytes. The fabrication of composite polymer electrolytes includes the addition of a salt and nanofillers (nanoparticles, nanoclays, nanorods or nanowires) in the host polymer matrix. It is noteworthy that the most critical requirement for the production of electrolytes based on polymer nanocomposites is the formation of the amorphous content that should improve the electrode/electrolyte interface in energy storage/conversion devices (Arya and Sharma, 2017) (Fig. 6).

The Applications of Polymer-Ceramic Nanocomposites in Biotechnology and Medicine

Biopolymer-based materials have many desirable properties that make them attractive for biotechnology applications, especially in the area of smart food packaging (Fig. 7). The development of such packaging materials offers significant economic and environmental advantages, because they are biodegradable and biocompatible. Additionally, these natural-based materials act not only as barriers, but also as scaffolds for the incorporation of additives in the form of antimicrobial agents, antioxidants and nutrients, which enhance their functionality. Although numerous biopolymers, such as carbohydrates, proteins, and lipids, have been studied as a base for eco-friendly packaging materials, carbohydrates are regarded as the most suitable for food applications due to their excellent film-forming and moderate mechanical and barrier properties (Zafar *et al.*, 2016). The most widely used method for improving agar-based materials is combining them with another component in order to obtain composite materials. It has been shown that the incorporation of nanoclay (Rhim, 2011), nanocellulose (Reddy and Rhim, 2014), or metallic nanoparticles (Arfat *et al.*, 2017) into agar can significantly improve the properties of the obtained nanocomposites. Also, if these nanofillers contain metals with a strong antimicrobial effect, like zinc (Lemire *et al.*, 2013), the resulting nanocomposite transforms into an active package with antimicrobial activity. The simplest approach in the production of the mentioned type of nanocomposites is adding a nanofiller to an agar solution prior to film formation. However, a reinforcing agent can sometimes be introduced into the agar matrix by in situ synthesis. This approach has been effective in the case of agar/hydroxyapatite (Hu *et al.*, 2016) and agar/gelatin/hydroxyapatite (Deng *et al.*, 2013) nanocomposites for biomedical applications, where hydroxyapatite was formed within an agar hydrogel by mineralization through electrophoretic deposition or immersion. A similar strategy could be employed for the production of mineral-impregnated agar films. Additionally, if the reinforcing minerals are zinc salts, the resulting nanocomposite could be improved both in a structural and functional sense. It has been shown that Zn-mineralized agar nanocomposite films could be used as affordable, eco-friendly, biodegradable, and antimicrobial food packaging materials. Their enhanced mechanical and light barrier properties, combined with functionality in terms of antimicrobial activity, facilitate the

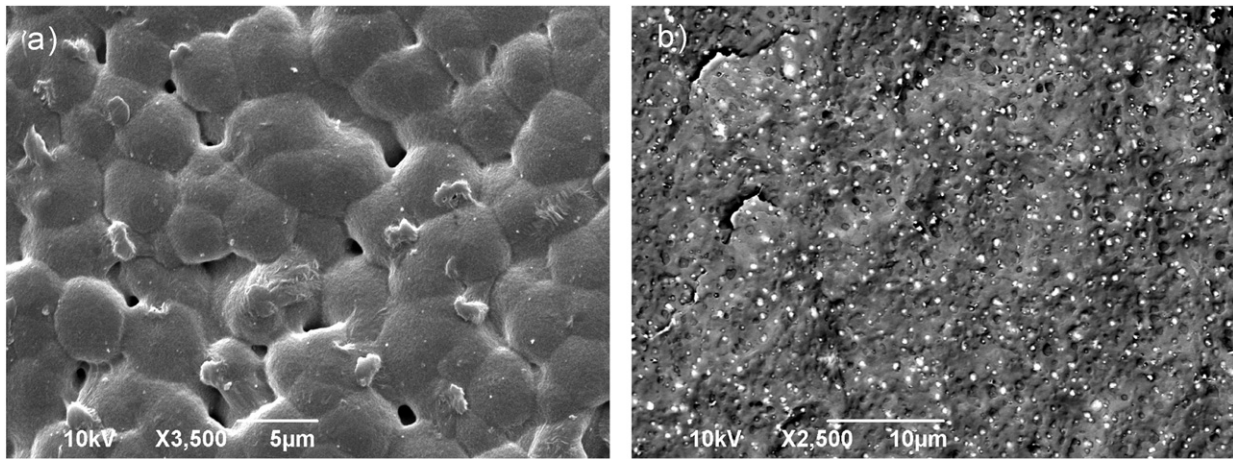


Fig. 6 Microstructures of various PVDF polymer-ceramic nanocomposites.

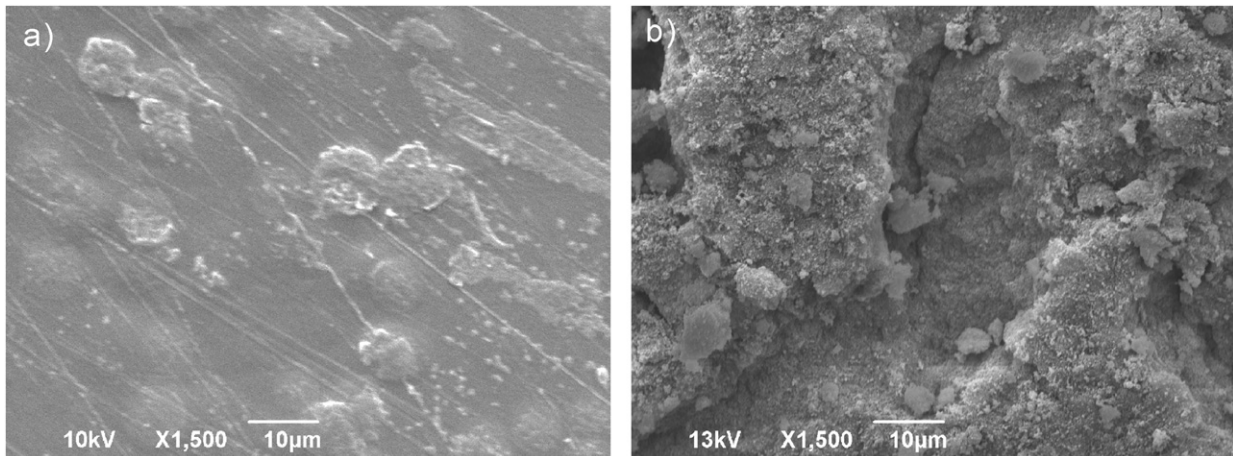


Fig. 7 Microstructure of agar and alginate-based nanocomposites for smart food packaging.

processing and handling procedures associated with packaging materials, which could improve packed food quality and ensure an extend shelf-life (Malagurski *et al.*, 2017a).

Another important material that can be used for the production of biopolymer-ceramic nanocomposites is alginate (Malagurski *et al.*, 2017b). Alginates are linear copolymers of 1–4 linked β -D-mannuronic acid (M) and α -L-guluronic (G) units, organized into homopolymeric (M- and G-blocks) and heteropolymeric (MG-blocks) regions. The most important characteristic of alginates, from a biomedical perspective, is the ability to selectively bind divalent metal ions and form biocompatible and hydrophilic hydrogels with wide biomedical applications. It has been shown that the mineralization of alginate in the presence of calcium and phosphate mineral precursors results in the formation of poorly crystalline hydroxyapatite, suitable for bone tissue engineering. Mineralized alginates have been studied as cell and drug delivery systems, as well. It has also been shown that two bimetallic (Zn/Cu) alginate-based nanocomposites, impregnated with a carbonate or a phosphate mineral phase, could be used as affordable and easy to produce antimicrobial materials (Malagurski *et al.*, 2018).

Polymer-ceramic nanocomposites have also been identified as a topic of interest in regenerative medicine, in the field of tissue engineering (Mozafari *et al.*, 2012). While some of these materials consist of calcium hydroxyapatite, phosphate, or a combination of poly(lactic acid) collagen and chitosan, others include conductive polymers as one of the materials facilitating communication with neural system for regenerative purposes. Although the utilization of conductive polymers in nanocomposite scaffold design is relatively new in tissue engineering applications and there are some difficulties associated with their fabrication, it has been shown that they are able to modulate the growth of endothelial, nerve, and chromaffin cells (Garner *et al.*, 1999; Valentini *et al.*, 1992; Kotwal and Schmidt, 2001).

Another application of polymer-ceramic nanocomposites in biomedicine includes polycaprolactone/SiO₂ for bone-bioerodible materials for skeletal tissue repair, PMMA/SiO₂ for dental application, shape memory polymers/SiC for medical devices used in the gripping or releasing therapeutics within blood vessels, etc. (Camargo *et al.*, 2009).

Polymer-Ceramic Nanocomposites for Environmental Protection and Remediation

It has been estimated that, in terms of weight, the disposed plastic waste accounts for 8% of the total amount of the world's solid waste. It is a huge environmental problem caused by the long-term degradation of disposed materials. Therefore, the utilization of recyclable raw materials for the unsaturated polyester (UPe) resin production can not only reduce the amount of solid plastic waste, but also leads to valuable market competitiveness, since it represents an alternative to the synthesis of more traditional composite materials. By incorporating modified inorganic nanoparticles in polymer matrices, new reinforced materials with integrated polymer matrix functionalities can be obtained. One of the reinforced materials with a wide range of industrial applications is UPe loaded with ceramic nanofillers (e.g., titanium oxide) (Srinivasa and Manonmani, 2014) and organochemically modified silicone oxide particles (Jastrz bska *et al.*, 2014; Wang *et al.*, 2014). It has been found that a significant improvement of mechanical and thermal properties of nanocomposite materials obtained by adding silica to a polymer is caused by strong interactions between silica nanoparticles and strong filler crosslinking. On the other hand, a good filler dispersion, stability and compatibility with the matrix can be obtained by chemical surface modification of hydroxyl groups with organo-silanes (Rusmirovic *et al.*, 2016). It should be mentioned that surface functionalization of nanostructured materials has appeared to be an effective way of modifying the material's surface properties towards achieving desired physical, chemical, or biological characteristics and the targeted response to the environment. This type of functionalisation enables incorporation of various functional groups, which further enhances the affinity for attaching a certain type of molecules to the material, by establishing specific bonds or electrostatic interactions. It has been shown that surface functionalisation of carbon nanotubes (CNTs) can largely influence the dispersibility of CNTs in polymer matrix. Namely, the addition of CNTs in polymer matrix can be important, since it yields materials that retain low deflections, as well as low specific stiffness. However, the application of CNTs is limited because of poor dispersion in solvents and polymers, due to strong Van der Waals interactions that lead to the formation of aggregates. A common method for improving dispersion is the chemical oxidative surface treatment or the functionalisation of nanotubes, which allows a covalent or a non-covalent bond between the nanotube and the composite matrix. It has been observed that vinyl modification of multi-walled carbon nanotubes can improve the overall properties of a recycled material and lead to the production of high-performance nanocomposite materials based on waste PET (polyethylene terephthalate) glycolysates (Tasic *et al.*, 2017). Furthermore, it has been proven that covalent functionalizations of the sidewalls of multi-walled carbon nanotubes (MWCNTs) can be an effective way to overcome solubility limitations and to achieve homogeneous dispersion by improving interfacial adhesion of filler in the host composite matrix. It is noteworthy that although this functionalization approach facilitates the distribution of MWCNTs in different media, the distortion of the structure and the defects on the sidewalls can be a consequence of a significant conversion of sp^2 hybridized carbon atoms into sp^3 in the carbon nanotube lattice (Brkovic *et al.*, 2017).

In the field of environment protection and remediation, there is a growing demand for the application of the fillers of natural origin to obtain recyclable and biodegradable nanocomposites (Fig. 8). Natural fillers, such as minerals, vegetal materials, reinforcements based on common elements, layered double hydroxides, and layered hydroxide salts, can be used for the fabrication of environment-friendly polymer-ceramic nanocomposites derived from plasticized polyhydroxyalkanoates (PHAs), saccharides, polylactide and poly (ϵ -caprolactone) (Camargo *et al.*, 2009). Renewable natural fillers, such as lignocellulosic materials, nanocrystalline cellulose (NC), and cellulosic fibers, are also often used together with nanoceramic reinforcement materials, for the development of composites based on thermosetting polymer matrices. The unique high crystalline and well-defined NC structure with one dimension in the nanometer range, as well as a high aspect ratio, high mechanical properties, rigidity, tensile strength (0.3–22 GPa), and modulus (138–150 GPa), makes NC a valuable filler in polymer-ceramic nanocomposites (Rusmirovic *et al.*, 2018). Although some of the major disadvantages of the NC-reinforcing filler include moisture absorption and dispersibility, in recent years, many techniques for chemical surface

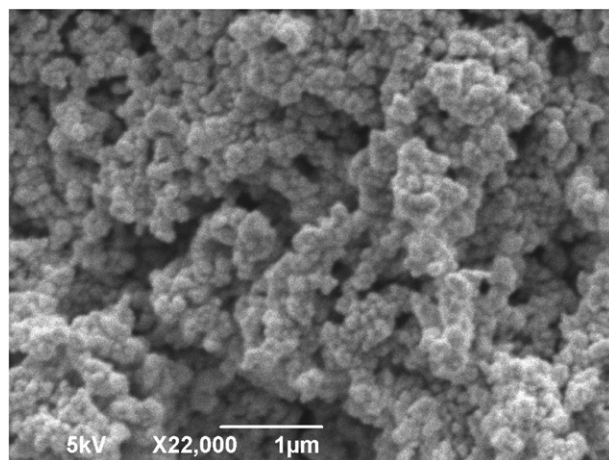


Fig. 8 Microstruture of NC-based nanocomposites.

modification of NC have been considered in order to improve dispersibility, compatibility, and bonding (interactions at the interface) with nonpolar polymer matrices in polymer-ceramic nanocomposites.

Another promising application of polymer-ceramic nanocomposites for environmental protection is the removal of carbon dioxide. The removal of carbon dioxide can be achieved via solution absorption, solid sorbents, membrane separation and cryogenic processing methods. Conventional physical sorbents include carbon sorbents, zeolite sorbents, carbon molecular sieves, metal-organic frameworks (MOFs), porous polymers and nanoclays (Wang and O'Hare, 2012). To overcome the problem of low carbon dioxide adsorption capacity at relatively low carbon dioxide partial pressure and the problem of lower selectivity toward carbon dioxide associated with physical sorbents, polymer-ceramic nanocomposites based on polymers with rich amine groups have been explored. Advances in this area include the development of polyaniline/multiwalled carbon nanotubes nanocomposites (Mishra and Ramaprabhu, 2012), polymer nanosieve membranes for CO₂-capture applications (Du *et al.*, 2011) and poly-ethylenimine-magadiite layered silicate nanocomposite sorbents for carbon dioxide capture (Vieira and Pastore, 2014).

Although a significant progress in processing, characterization and fabrication of nanostructured materials has opened up great opportunities for engineering the properties of polymer-ceramic nanocomposite systems, in terms of sustainability, additional research efforts are required toward developing novel polymer nanocomposites based on clean, sustainable, and renewable energy sources.

Conclusion

The need for novel materials with an advanced functionality increases, as the market of the materials that can be used in various converging technologies expands. The development of polymer-ceramic nanocomposites is an evolving area of interdisciplinary research, motivated by new emerging technologies, such as the Internet of Things. The unique functionality of these nanostructures has enabled their applications in numerous devices such as: micro and nano-electro-mechanical systems (MEMS/NEMS), sensors, microactuators, surface acoustic wave devices, polymer electrolyte membrane fuel cells, switches, thermistors, resonators and filters, electrooptic devices, etc. They are also used in various fields of biotechnology and medicine, as well as for environmental protection and remediation. Polymer-ceramic nanocomposites have advantages over the other advanced materials due to their high toughness, good transparency, easy formability, small weight and low cost. The possibility to tailor their structure at the nanoscale has opened up great opportunities in the engineering of the properties of polymer-ceramic nanocomposite systems. The fabrication of low-cost biodegradable nanocomposites will significantly contribute to the quality of life and environment. Moreover, the development of eco-friendly polymer-ceramic nanocomposites will reduce the amount of solid waste, improve package manufacturing capabilities and reduce the overall logistics burden to users. It is expected that the future research will be focused on the development of processing techniques toward enhancing the dispersion of ceramic fillers, reducing the agglomeration and increasing the interface properties between the ceramic reinforcement and the matrix. In order to solve these problems, the reliance on the principles of directed synthesis and the development of modeling and simulation tools enabling the study of the structure-properties relationship will be beneficial.

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Metal Particles as Additives in Ceramic Composite Materials: A Review of Mechanical Properties and Their Origin

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Introduction

There are many industrial applications of ceramic material such as for cutting tools, wear parts, seals for water pumps, aerospace, filtering material such as a membrane for separation, light weight structural materials, and drug delivery (Tang *et al.*, 2004; Wang *et al.*, 2009; Xu *et al.*, 2016; Ali *et al.*, 2017a). Ceramic materials are characterized by their wear resistance, chemical stability, and high degree of hardness and heat resistance (Chmielewski and Pietrzak, 2007; Ali *et al.*, 2017b). However, the inherent brittleness of ceramic materials pose a limitation to their applications (Chen and Tuan, 2001; Tuan and Chou, 1996). In recent years, many attempts have been made to improve the mechanical properties such as the fracture toughness of structural ceramics with additional re-enforcing phases, known as the secondary phase. For instance, improvement was observed in the fracture toughness of alumina (Al_2O_3) ceramic composites from 5.21 to 5.26 $\text{MPa m}^{1/2}$ by adding 15–25 vol% niobium (Nb) to alumina matrix and fabricated using the hot-pressing method at 1550°C for 5 min. Enhancement was also seen in wear resistance due to limited thermal expansion mismatch with respect to alumina matrix and the ductility of Nb which leads to strongly bonded Nb particles with matrix (de Portu *et al.*, 2007; Wenzel and Aneziris, 2011). Factors that affect fracture toughness are the uniformity of the metal phase distribution, its quantity, particle size and shape, its physical properties, as well as the metal-ceramic interface properties. The addition of tantalum (Ta) metal in the range of 5–15 vol% into zirconia (ZrO_2) ceramic using the pressureless sintering process was prepared in the work of Smirnov and Bartolomé (2014). From this work, it was found that the fracture toughness of ZrO_2 matrix was improved from 12 to 14 $\text{MPa m}^{1/2}$. This significant improvement was attributed to the uniformly distributed metal particles in the zirconia matrix. It was noted that the metal phase was able to absorb the crack propagation energy during fracture and could enhance crack bridging and deflection as well as relaxation of stress near the crack tip (Alman and Hawk, 2001; Chmielewski *et al.*, 2012; Lane *et al.*, 1998; Moya *et al.*, 2008; Smirnov and Bartolomé, 2014; Szafran *et al.*, 2007). In addition, the metal particle's shape plays a significant role in the extent of fracture toughness improvement of the metal-ceramic composites. In the work of Vekinis *et al.* (1997) short nickel fibers in concentration from 0 to 24 vol% were used as the reinforcement in an alumina ceramic matrix. The nickel fibre lengths and diameter were 0.3–0.8 mm and 50 μm respectively. The in-situ reduction method was utilized during sintering which lead to an overall increase in fracture toughness of the alumina from 2.37 to 2.85 $\text{MPa m}^{1/2}$. This was attributes to crack bridging provided by the plastic deformation of metal phase (Vekinis *et al.*, 1997).

There are three main types of ceramic–metal composites. The first type is ceramic matrix composites with a continuous ceramic network. The quantity of ceramic is typically larger than that of the metal for this type of ceramic matrix composite. The second type is metal matrix composites with a continuous metal network. In this case, the quantity of the metal is usually higher than that of the ceramic. The third type is the interpenetrating network composites, where both components are continuous. Benefits of using a higher ceramic content network include the higher degree of hardness, load bearing capacity and Young's modulus in comparison to metal based matrix composites (Winzer *et al.*, 2011; Yin *et al.*, 2014). Many researchers (Cesari *et al.*, 2006; Huang *et al.*, 2007; Tekeli, 2005; Zuo *et al.*, 2007) have noted the limit in performance that a single ceramic material can provide in the composite structure. Recently, there is much investigation focus on multiphase ceramic materials developed from the research conducted of single-component ceramic composite material (Rong *et al.*, 2007a). In addition, the properties of fundamental materials and technological applications such as coating, fuel cells, heterogeneous catalysis, microelectronics and optoelectronics are dependent on in-depth understanding of the ceramic/metal particles interfaces (Moya *et al.*, 2007). Many authors (Rosso, 2006; Moya *et al.*, 2007) have reviewed ceramic/metal composite materials under different topics. Rosso (2006) reviewed method and properties of ceramic and metal matrix composites. This review noted that the advancement of materials engineering is related to new materials and processing technologies, economical manufacturing processes, with application to diverse markets, and utilising system solutions. Moya *et al.* (2007) reviewed the challenge of using ceramic-metal nano and micro composites in different fields. This review presented the opportunities and challenges for ceramic-metal composites in different fields of science and technology. Although much research work has been conducted on ceramic composite materials, there has yet to be any research studies that perform a detailed comparison of these works for the identification of technical areas for improvement. This

review will aid the further development in the area of ceramic-metal composite materials. Therefore, this is the focus of this article, to review previous research work in this area to aid further research focused on the development of ceramic-metal composites. The effects of metal particle additives on the mechanical and other properties such as thermal shock and self-lubrication of ceramic materials is presented here. This paper also reviews the toughening mechanisms, which have been found lead to the enhancement of their mechanical properties.

Mechanical Properties of Ceramic Materials

The majority of research on the development of mechanical properties in ceramic matrix composites has been conducted over the last 50 years. In the work of Danzer, it was noted that composites produced by the addition of metal particles to ceramic materials have been found in many published research works to have increased toughness and strength (Danzer, 2014). In the text below, a review of the improvements in the mechanical properties of ceramic materials using metal particles additives and the mechanisms behind these are presented.

Effect on Mechanical Properties

It is possible to increase the reliability of ceramic materials by reducing flaws (Ekström, 1993; Sato *et al.*, 2006). Another way to improve the mechanical properties of ceramic materials lies in the addition of metal within the brittle ceramic matrix (Rong *et al.*, 2007a,b; Rubinstein and Wang, 1998). Cartz (1988) reported the influence of copper particles addition on the mechanical properties of alumina ceramics sintered at 1550°C for 1 h using the hot-press method. The study showed that fracture toughness, density and bending strength improve significantly for the alumina ceramics. Increasing copper (Cu) content resulted in fracture toughness, density and bending strength improvement. Due to the low melting temperature of Cu (1085°C) compared with the alumina matrix (2072°C), the transfer of solute will accelerate during the sintering process which leads to an increase in composite density and strength. Wang *et al.* (2009) presented a study on the effects of molybdenum Mo in concentrations from 0% to 10% volume fraction on the zirconium diboride (ZrB₂) ceramic composites sintered at 1950°C using the hot-pressing process. It was found that the addition of Mo metal particles improves of the mechanical properties of ZrB₂ ceramic composites. Bending strength increased from 424 to 450 MPa and the fracture toughness increased from 4.52 to 7.98 MPa m^{1/2}. The improvement in mechanical properties of ZrB₂/Mo ceramic matrix composites were attributed to the formation of MoB phase and reduced grains size (Wang *et al.*, 2009). There are three main reasons in the improvement of the strength and fracture toughness for the ZrB₂/Mo composites. The first is the high relative density enhancing the strength and fracture toughness of composites. The second is the small size particle grain providing a larger grain interface, resulting in composite toughening. The third is that the enhanced mechanical properties induce the Mo grains to change the fracture mode of the ZrB₂/Mo composites from a fully intergranular mode to a mixed inter/transgranular mode (Wang *et al.*, 2009). However, there is a decrease in the bending strength and toughness of the fracture when the amount of Mo exceeds 10%. This may be related to the adverse reactions between Mo and ZrB₂ at these higher concentration. At lower concentrations, the reaction reinforcement results in the interfacial bonding between ZrB₂ and Mo phases. This cause the cracks to break into ZrB₂ grains, leading to intergranular cracks rather than propagated cracks along the interfaces (Wang *et al.*, 2009). Chou and Tuan (1995) presented toughening and strengthening of alumina ceramics with silver inclusions using pressureless sintering technique at 1600°C and 1700°C. The study showed that both the toughness and strength improved due to the silver inclusions. The enhancement in toughness and strength attributed to the plastic deformation of silver and the matrix grain refinement. Wenzel and Aneziris (2011) reported the preparation of ceramic composites comprising magnesia partially stabilized zirconia (Mg-PSZ) and 10–30 vol% metastable austenitic Cr-Ni steel (TRIP-steel) using slip casting technology. It was revealed that the fracture strength of ceramic composites with 20 vol% of TRIP-steel increased by 43% in comparison with pure Mg-PSZ. The improvement in fracture strength of ceramic composite could be attributed to transformation from austenite to α -martensite, providing crack tip shielding. Li *et al.* (2003) studied the fabrication of alumina/nickel (Al₂O₃/Ni) nanocomposites by a chemical method and hot-pressing technique sintered at 1450°C for 1 h using aluminum nitrate nonahydrate (Al(NO)₃ · 9H₂O) and nickel oxide (NiO) as starting materials. The study showed that the toughness was enhanced by 79% and the strength increased by 26% with addition of Ni at 5 vol% in contrast with the pure Al₂O₃ (see Fig. 1). The enhancement in mechanical properties were related to the mechanisms of metallic grain pullout, crack branching, and crack deflection.

Li *et al.* (2003) reported that the strength increase of the Al₂O₃/Ni composite could be correlated with a decrease in the grain size of the Al₂O₃ matrix. When the Ni content was higher, there is an increase in the strength of the composites that was attributed to increased densification of composite (Li *et al.*, 2003). The fracture strength (σ_f) of brittle material is expressed as per the following Eq. (1) according to the Griffith theory,

$$\sigma_f = \left(\frac{1}{Y}\right) \frac{K_{IC}}{C^{1/2}} \quad (1)$$

where K_{IC} , Y and C are the fracture toughness, geometrical parameter and one-half the width of the initial flaw, respectively (Li *et al.*, 2004; Lu *et al.*, 2000). In dense polycrystalline materials the C factor is proportional to the grain size. Typically when the grain size becomes smaller, the fracture strength shows an increase. Techniques used to discover the morphology features of microstructure (grain size, uniformity, grain boundary, and porosity) of ceramic composite materials include FESEM, SEM, optical

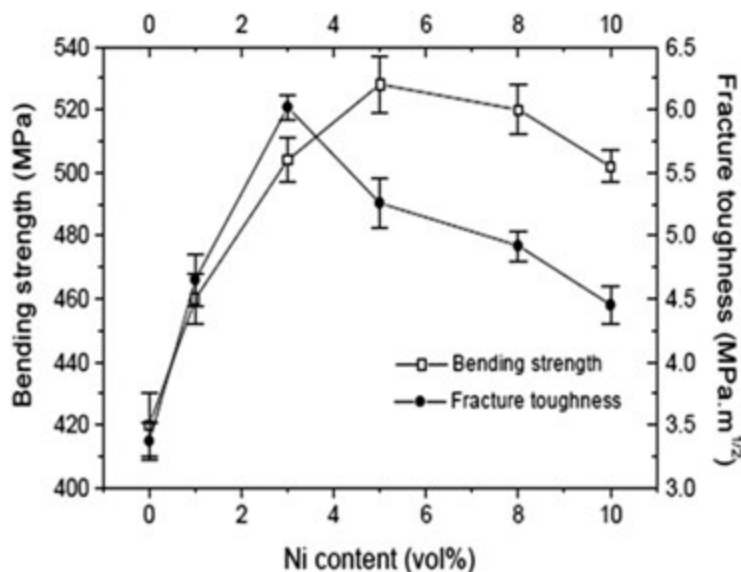


Fig. 1 Effect of Ni content on the bending strength and fracture toughness of $\text{Al}_2\text{O}_3/\text{Ni}$ ceramic composites. Reproduced from Li, G.-J., Huang, X.-X., Guo, J.-K., 2003. Fabrication, microstructure and mechanical properties of $\text{Al}_2\text{O}_3/\text{Ni}$ nanocomposites by a chemical method. *Materials Research Bulletin* 38 (11), 1591–1600.

microscope, and TEM (Ji and Yeomans, 2002; Li *et al.*, 2003). **Fig. 2** presents the SEM micrographs of the surface of fracture of $\text{Al}_2\text{O}_3/\text{Ni}$ composite. It can be seen that the matrix grain size of $\text{Al}_2\text{O}_3/\text{Ni}$ composite is finer compared with the monolithic Al_2O_3 , indicating the extent of restriction in grain growth of Al_2O_3 upon Ni addition. **Fig. 3** shows the relationship between the fracture strength and grain size for $\text{Al}_2\text{O}_3/\text{Ni}$ composites.

Chen and Tuan (1999) reported on the addition of 5 vol% of nano-nickel particles on mechanical properties of alumina (Al_2O_3) ceramic matrix sintered at 1400°C for 2 h using pressure less sintering technique. The study revealed that the strength of $\text{Ni}/\text{Al}_2\text{O}_3$ nanocomposite depends strongly on the grain size of the ceramic matrix. After adding Ni, the grain size of ceramic matrix decreased from 750 to 450 nm (see **Fig. 4**) while the strength and fracture toughness were increased from 390 to 526 MPa and from 3.6 to 4.2 $\text{MPa m}^{1/2}$ respectively. This improvement in the mechanical properties of these ceramic composites is widely attributed to microstructural refinement (Chen and Tuan, 1999).

Mashhadi *et al.* (2011) studied the effect of Al additions from 0 to 5 wt% on boron carbide-titanium diboride ($\text{B}_4\text{C}-\text{TiB}_2$) composites sintered at 2050°C and 2150°C using the pressureless sintering process. It was found that with an increase in Al content, the mechanical properties of $\text{B}_4\text{C}-\text{TiB}_2$ composites are significantly enhanced. The maximum values of fracture toughness, hardness, elastic modulus, and fracture strength were measured at 6.2 $\text{MPa m}^{1/2}$, 35 GPa, 500 GPa, and 450 MPa respectively. The recorded improvement in mechanical properties were attributed to the increase in relative density with less grain growth (see **Fig. 5**).

Yin *et al.* (2014) presented the effects of adding nickel and cobalt to Al_2O_3 ceramic matrix to produce ceramic composite for tool materials with excellent mechanical properties. The study noted that the improvement in mechanical properties such as fracture toughness and flexural strength of ceramic composites with metallic phase was attributed to crack deflection, intragranular grain failure, crack bridging by metal particles, lower residual tensile stress in the alumina matrix, filled pores, and enhancement in strength of interfacial bonding. Latifi *et al.* (2014b) reported the influence of Ni and iron particles on the boron carbide (B_4C) and 10 vol% nano-titanium diboride (TiB_2) ceramic composites properties using the cold pressing method. It is found that addition of Ni and Fe enhanced the values of Young's modulus, hardness, and fracture toughness (see **Fig. 6**). These improvements in mechanical properties were attributed to an increase in density which comes from the improvement of condensation procedure due to the addition of metal phase to ceramic composites during the sintering process. Formation of liquid phases such as nickel boride (Ni_3B) and iron boride (FeB) with low melting point helps to reduce the excessive grain growth, porosity value, and boundary mobility (Ali *et al.*, 2016).

Different methods of ceramic/metal composites preparation may lead to different microstructure, hence various properties. Chmielewski and Pietrzak (2007) studied preparation of alumina (Al_2O_3) + 25 vol% Cr ceramic composites using pressure less sintering with sintering temperature of 1600°C for 1 h and hot-pressing with pressure of 30 MPa, sintering temperature of 1400°C for 1 h. The study showed that using hot-pressing process provided good mechanical properties of Al_2O_3 -Cr composites compared with pressure less sintering process due to lower porosity and finer grains sizes of Al_2O_3 after hot-pressing. The hardness and bending strength were 8.78 GPa and 277.5 MPa respectively using pressure less sintering method while the hardness and bending strength were recorded at 9.51 GPa and 314.8 MPa respectively from using hot-pressing method.

Zuo *et al.* (2007) reported on the preparation of $(\text{Al}_2\text{O}_3 + \text{Ni})$ composite, $(\text{Al}_2\text{O}_3 + \text{Ni})/\text{Ni}$ and $\text{Al}_2\text{O}_3 + (\text{Al}_2\text{O}_3 + \text{Ni})/\text{Ni}$ laminated materials using the aqueous tape casting and hot-pressing technique, as shown in **Fig. 7**. This study showed that the

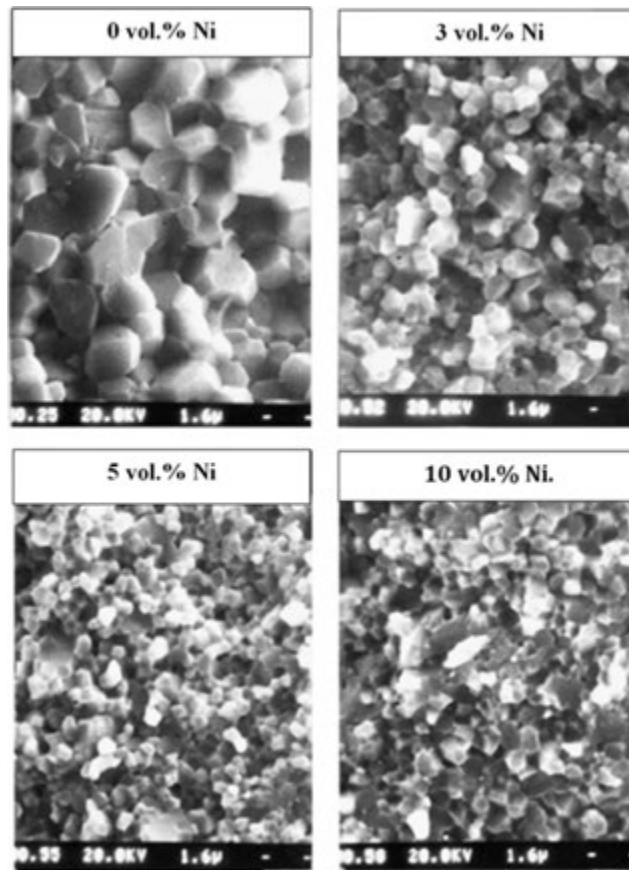


Fig. 2 SEM micrographs of fracture surface of $\text{Al}_2\text{O}_3/\text{Ni}$ composite with different ratios of Ni. Reproduced from Li, G.-J., Huang, X.-X., Guo, J.-K., 2003. Fabrication, microstructure and mechanical properties of $\text{Al}_2\text{O}_3/\text{Ni}$ nanocomposites by a chemical method. Materials Research Bulletin 38 (11), 1591–1600.

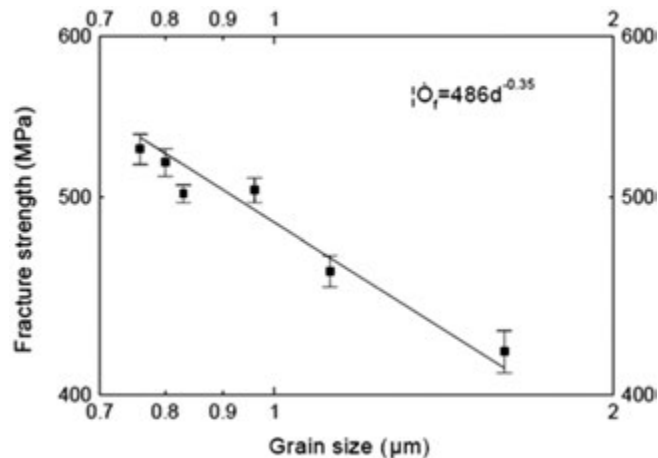


Fig. 3 Relationship between the fracture strength and grain size for $\text{Al}_2\text{O}_3/\text{Ni}$ composites. Reproduced from Li, G.-J., Huang, X.-X., Guo, J.-K., 2003. Fabrication, microstructure and mechanical properties of $\text{Al}_2\text{O}_3/\text{Ni}$ nanocomposites by a chemical method. Materials Research Bulletin 38 (11), 1591–1600.

resulting fracture toughness and strength of $(\text{Al}_2\text{O}_3 + \text{Ni})$ were higher than those of monolithic Al_2O_3 . The toughness of $\text{Al}_2\text{O}_3 + (\text{Al}_2\text{O}_3 + \text{Ni})/\text{Ni}$ and $(\text{Al}_2\text{O}_3 + \text{Ni})/\text{Ni}$ were higher than not only monolithic Al_2O_3 , but also that of $(\text{Al}_2\text{O}_3 + \text{Ni})$ with the same thickness and number of layers. These improvements in mechanical properties were attributed to the toughening mechanism of the composite laminated structure with the metallic second phase providing crack and crack deflection by residual stress. The

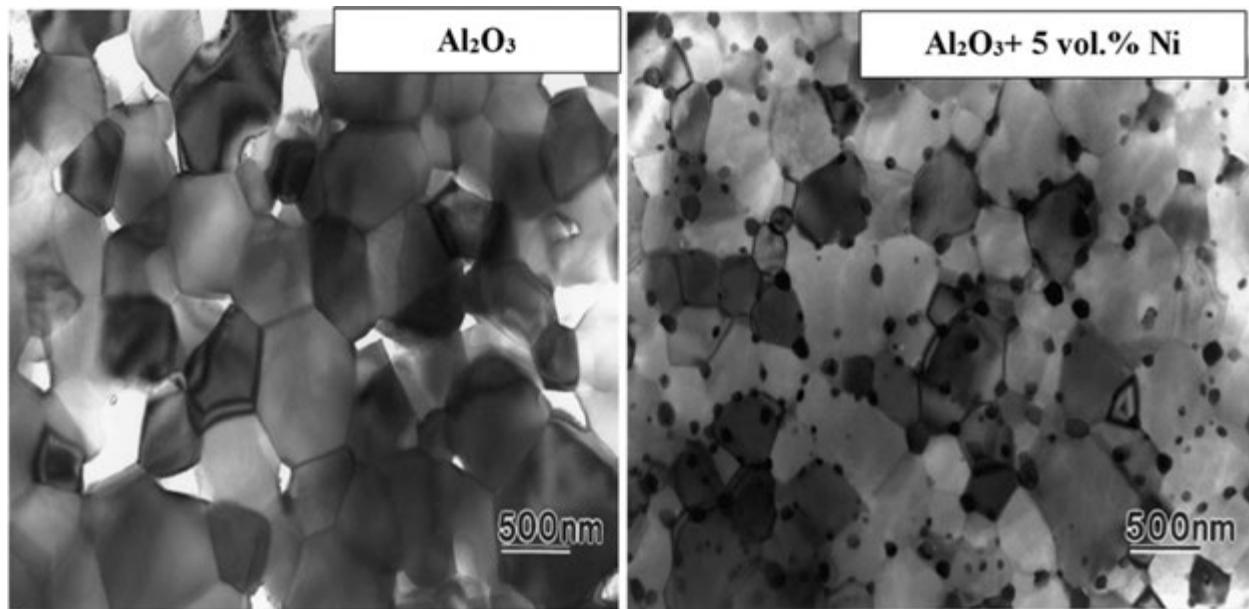


Fig. 4 TEM images of Al_2O_3 and $\text{Al}_2\text{O}_3/\text{Ni}$ nanocomposite samples sintered at 1400°C for 2 h. Reproduced from Chen, R., Tuan, W., 1999. Pressureless sintering of $\text{Al}_2\text{O}_3/\text{Ni}$ nanocomposites. *Journal of the European Ceramic Society* 19 (4), 463–468.

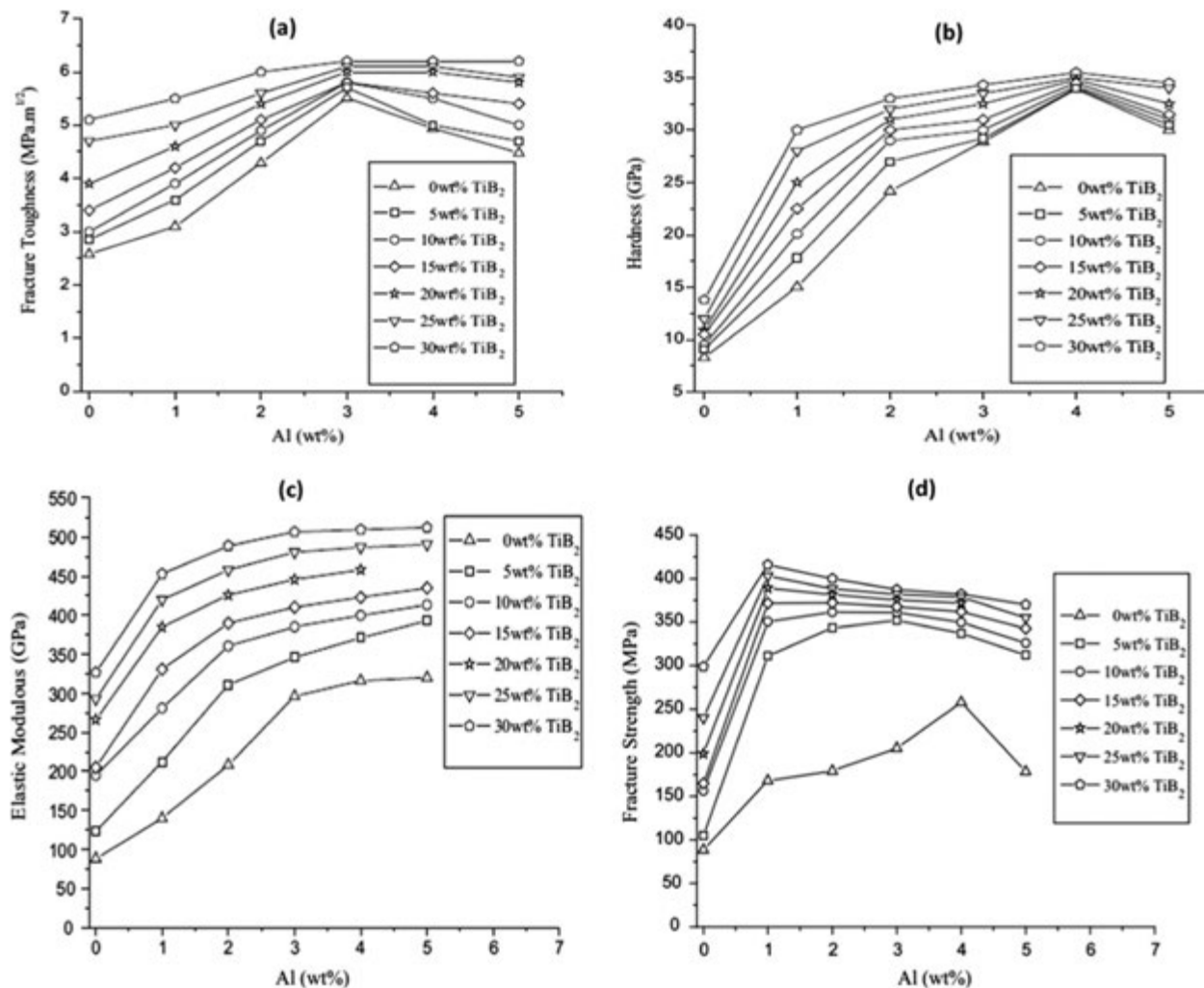


Fig. 5 Variation of mechanical properties of $\text{B}_4\text{C}-\text{TiB}_2$ ceramic composites with Al ratios: (a) fracture toughness, (b) hardness, (c) elastic modulus, and fracture strength. Reproduced from Mashhadi, M., Taheri-Nassaj, E., Mashhadi, M., Sglavo, V.M., 2011. Pressureless sintering of $\text{B}_4\text{C}-\text{TiB}_2$ composites with Al additions. *Ceramics International* 37 (8), 3229–3235.

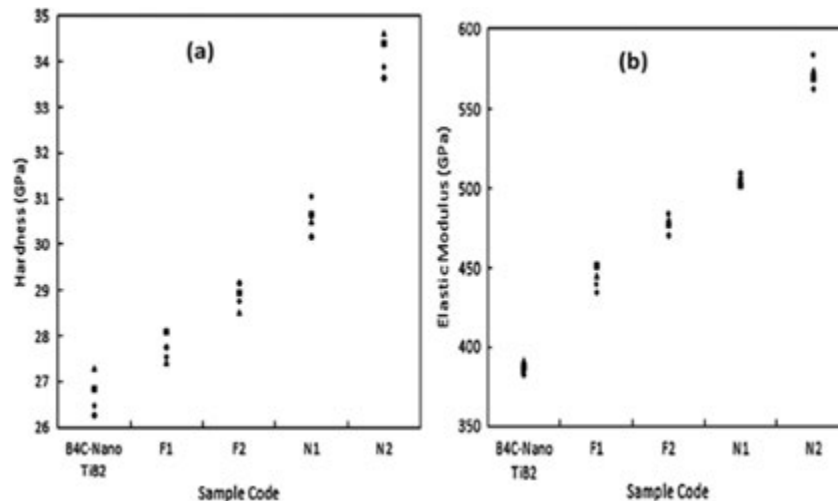


Fig. 6 Variation of mechanical properties with metal additives; F1, F2 (1.5–2.5 Fe vol%) and N1, N2 (1.5–2.5 Ni vol%): (a) hardness and (b) elastic modulus of B₄C ceramic composites. Reproduced from Latifi, H., Moradkhani, A., Baharvandi, H., Martikainen, J., 2014a. Fracture toughness determination and microstructure investigation of a B₄C–NanoTiB₂ composite with various volume percent of Fe and Ni additives. *Materials & Design* 62, 392–400.

highest toughness recorded from the Al₂O₃ + (Al₂O₃ + Ni)/Ni laminated materials was 16.10 MPa m^{1/2} which is significantly higher compared with that of monolithic Al₂O₃ (3.47 MPa m^{1/2}). The toughness and strength of (Al₂O₃ + Ni)/Ni with three layers and layer thickness ratio of 2 mm were 12.42 MPa m^{1/2} and 417.41 MPa respectively compared with the lower toughness (3.47 MPa m^{1/2}) and strength values (354.41 MPa) of monolithic Al₂O₃.

In conclusion, the metal particles, whether in nano or microscale, play an important role in providing the toughening mechanism such as ductile particle bridging and crack deflection whereby the ductile particles enhance the mechanical properties of ceramic composite. The preparation methods of ceramic composites also play a significant role in producing different microstructure hence different mechanical properties.

Table 1 shows the effect of adding metal particles on the mechanical properties of ceramic matrix composite.

Effect on Other Properties

This section reviews the a range of other properties of the ceramic composites self-lubrication and thermal shock resistance that are relevant for specific final applications.

Self-lubrication for ceramic composite

The addition of small amount of metal particle into ceramic materials can make them self-lubricating. The main disadvantage of using cooling lubricants with ceramic materials is that it incurs extra costs in the machining process. Moreover, the use of cooling lubricant is hazardous to the environment. Cutting tools with a self-lubricating property could be a replacement for standard machining processes which require cooling lubricant fluids for operation (Broniszewski *et al.*, 2013). In this case, there are several types of materials with a self-lubricating property such as Au, Ag, MoS₂, graphite and Mo that could be used within the ceramic matrix composite to replacement conventional lubricants used for standard machining processes (Kong *et al.*, 2014). Under loading, the compressive stress decreases with an increase in the volume fraction of molybdenum in the ceramic matrix. The structure of MoO₃ is similar to graphite, formed as a result of molybdenum oxidation at the machining temperature (Broniszewski *et al.*, 2013). Graphite is commonly used to serve as a solid lubricant, see graphite structure in Fig. 8. There is a decrease in the frictional coefficient between the machined material and cutting edge due to the presence of this material. Hence, self-lubricating ceramic materials may reduce environmental pollution and cost of operation (Broniszewski *et al.*, 2013). The in-plan atoms are linked with strong covalent chemical bonds whereas the sequent planes are linked with weak Van der Waals bonds. This structure allow for sliding of the sequent planes at low values of stress during machining (Broniszewski *et al.*, 2013). The main disadvantage of using cooling lubricants in the ceramic materials is that it incurs extra costs to the machining process. Moreover, the use of cooling lubricant is hazardous to the environment. In conclusion, the cutting tools with self-lubricating property can provide an important replacement tool material for standard machining process which traditionally have required cooling lubricant fluids for operation.

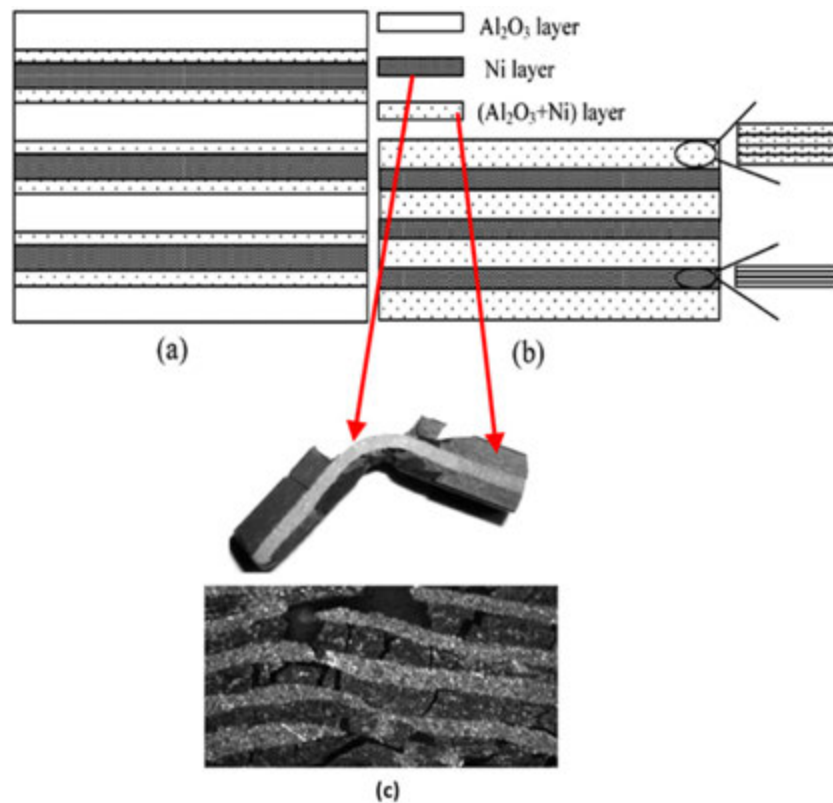


Fig. 7 Laminated materials: (a) $\text{Al}_2\text{O}_3 + (\text{Al}_2\text{O}_3 + \text{Ni})/\text{Ni}$ laminar, (b) $(\text{Al}_2\text{O}_3 + \text{Ni})/\text{Ni}$ laminar and (c) optical graph of laminated materials after calculating fracture strength. Reproduced from Zuo, K.H., Jiang, D.L., Lin, Q.L., Zeng, Y.-P., 2007. Improving the mechanical properties of $\text{Al}_2\text{O}_3/\text{Ni}$ laminated composites by adding Ni particles in Al_2O_3 layers. *Materials Science and Engineering: A* 443 (1), 296–300.

Table 1 Effects of metal particles addition on the mechanical properties of ceramic matrix composite

Composite materials	Metal powder vol%	Process	Properties
$\text{Al}_2\text{O}_3 + \text{Cu}$	(3–9) vol% Cu	Hot-pressing	Improvement in the bending strength and toughness (Rong <i>et al.</i> , 2007a)
$\text{ZrB}_2 + \text{Mo}$	(10) vol% Mo	Hot-pressing	Increased in fracture toughness from 4.52 to 7.98 $\text{MPa}/\text{m}^{1/2}$; and increased bending strength from 424 to 450 MPa (Wang <i>et al.</i> , 2009)
$\text{Al}_2\text{O}_3 + \text{Mo}$	(20–30) vol% Mo	Pressureless sintering	Higher hardness and fracture toughness (Konopka <i>et al.</i> , 2003)
$\text{Al}_2\text{O}_3 + \text{Ni}$	(5 vol% Ni) after reducing Al_2O_3 and NiO or NiAl_2O_4	Pressureless sintering	Enhanced toughness attributed to crack bridging or microcrack toughening mechanisms (Tuan, 1995)
$\text{Al}_2\text{O}_3 + \text{Cu}$	(5) vol% Cu	Hot-pressing	Enhanced toughness, increased thermal conductivity, decreased Young's modulus and slightly increased strength compared with monolithic alumina (Wang <i>et al.</i> , 2001)
$(\text{Al}_2\text{O}_3 + \text{ZrO}_2) + \text{Ni}$	(5–15) vol% Ni after sintering	Pressureless sintering	Increased toughness, strength and transformation ability of ZrO_2 (Chen <i>et al.</i> , 2000)
$\text{Al}_2\text{O}_3 + \text{Mo}$	(10) vol% Mo	Hot-pressing	Strength and the toughness of the dense composites increased 26% and 32% respectively relative to the non-reinforced ceramic (Wang, 1998)
$\text{B}_4\text{C}-\text{NanoTiB}_2$	0, 1.5 and 2.5 vol% (Ni)	Cold pressing	Improved density, Young's modulus, hardness and fracture toughness (Latifi <i>et al.</i> , 2014a)

Thermal shock resistance

Hasselman in (1969) introduced classic theory that explains the thermal shock behaviour of brittle ceramics. The classic work of Hasselman showed that opposing property requirements prevail, depending on whether the material is required to be resistant to crack initiation (for which high strength and low stiffness are essential) or resistant to strength degradation following a severe thermal shock (in which case low strength and high stiffness are beneficial). The theory described that opposing property requirements prevail. One example is whether the material is required to strengthen degradation after severe thermal shock or to

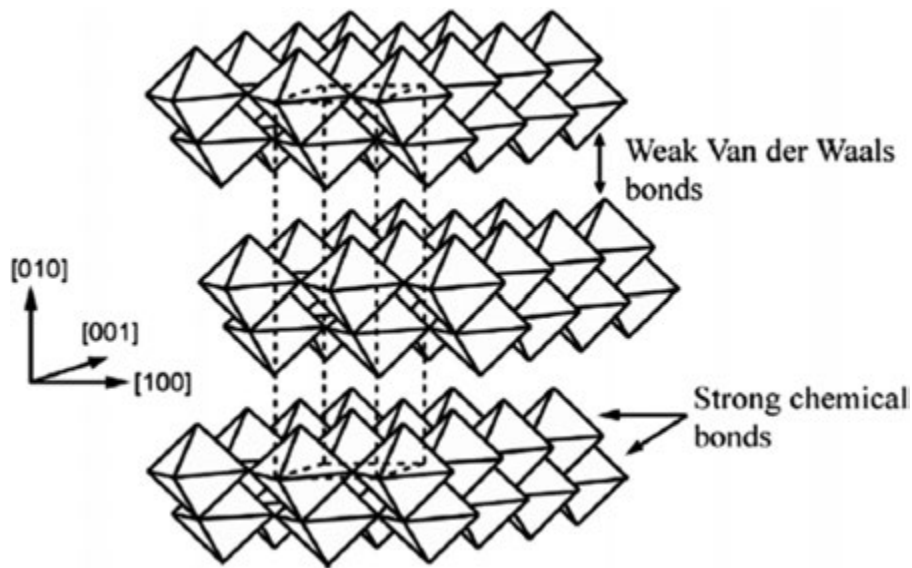


Fig. 8 Graphite structure showing strong in-plane and weak inter-plane bonds. Reproduced from Broniszewski, K., Wozniak, J., Czechowski, K., Jaworska, L., Olszyna, A., 2013. Al_2O_3 -Mo cutting tools for machining hardened stainless steel. *Wear* 303 (1–2), 87–91.

become resistant after initiation of cracks. In addition, this theory compares the thermal shock behaviour of ceramics in terms of their mechanical and physical properties (Aldridge and Yeomans, 1999; Wang *et al.*, 2001).

The findings showed that the thermal shock resistance of the monolith ceramic materials was lower than the hot pressed ceramic composite. Meanwhile, the behaviour of sintered composite was like a typically low strength refractory ceramic. Hence improving the resistance to thermal shock for ceramic materials in certain harsh environments is a significant achievement. The rate of transmitting heat across the brittle solids is particularly important for ceramic composites with weak thermal shock behaviour. The thermal gradient within the solid can be significant. This occurs due to excessive thermal accumulation that causes the formation of large thermally induced stresses. Finally, it ends with catastrophic failure and deterioration of their service performance. In fact, the thermal shock resistance of ceramic materials is also related to their thermal conductivity. It is noted that materials with a higher thermal conductivity have better resistance to thermal shock because they are able to reduce interior temperature gradients and thermal stress. However, the thermal stress generated during severe thermal quenching can still readily damage these materials due to effect of thermal gradient shock.

Wang *et al.* (2001) studied the effect of adding 5 vol% of copper particles on the thermal shock behaviour of alumina ceramic composites using the hot- pressing method. The ceramic composites were sintered at 1550°C . A 5 vol% of copper particles were added to the alumina composite which leads to improvement in toughness, increased thermal conductivity, increased flexural strength and a higher resistance to thermal shock compared to pure alumina. The enhancement in mechanical properties such as fracture toughness were attributed to crack deflection. Internal stress due to mismatch in coefficients of expansion between Al_2O_3 and Cu leads to microcrack blunting and arrest. Thus the composites has a fracture toughness about 15% more than the pure alumina. In conclusion, the addition of metal particle have important effect on enhancement of thermal shock of ceramic composite because it helps to reduce interior temperature gradients and thermal stress.

Effect on Toughening Mechanism of Ceramic Composites

There are several methods to improve the toughening mechanisms of ceramic composites. One of the methods to increase the strength and fracture toughness of ceramic material is to mix the metallic second phase into the ceramic matrix (Kafkaslıoğlu and Tür, 2016; Liu and Tuan, 1997; Sbaizero and Pezzotti, 2001; Ali *et al.*, 2017c,d). The most effective toughening mechanism is known as crack bridging (Zuo *et al.*, 2007). By adding metal particles into the ceramic matrix, the crack is bridged (Smirnov and Bartolomé, 2014). The other toughening mechanisms include enhanced plastic deformation and crack deflection (Ji and Yeomans, 2002). These two mechanisms are known for enhancing the toughness (Chou and Tuan, 1995) because the crack driving force is reduced at the crack tip (Gu *et al.*, 2006). The common ways of enhancing the fracture resistance of the ceramic matrix are a combination of mechanisms including (i) bridging of the crack by the ductile phase (Clegg and Paterson, 2004) such as use of fibers or circular grains behind the crack face (Boch and Niepce, 2010; Lalande *et al.*, 2002) (ii) deflection of the crack by the ductile phase (see Fig. 9), and (iii) ductile rupture of the metallic phase at the crack tip (Alman and Hawk, 2001; Chen and Tuan, 2001; Liu *et al.*, 2013; Rösler *et al.*, 2007).

One important factor for consideration in the toughening process is the mechanism of consuming fracture energy. This mechanism weakens the driving power of the crack tip and able to reduce the propagation of cracks (Smirnov and Bartolomé,

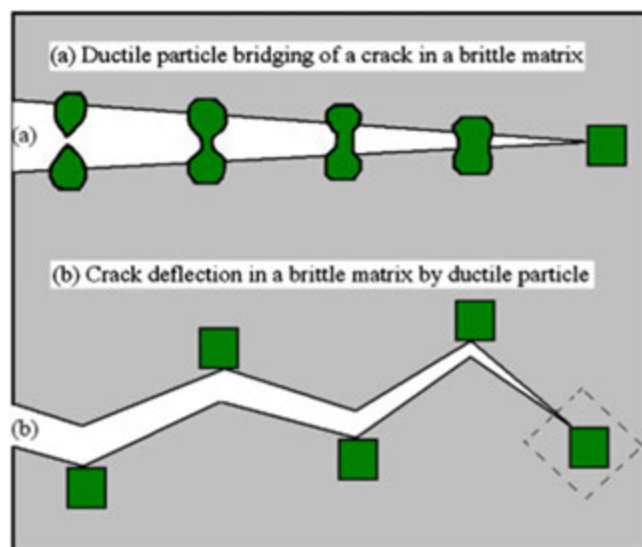


Fig. 9 The mechanisms of toughening using ductile particles in ceramic composite, (a) ductile particle bridging, (b) crack deflection by ductile particle. Reproduced from Liu, Y., Zhou, J., Shen, T., 2013. Effect of nano-metal particles on the fracture toughness of metal–ceramic composite. *Materials & Design* 45, 67–71.

2014). For the mechanism to occur, the energy that is concentrated at the crack tip is dissipated to produce higher toughness. When the force of stress at the crack tip is reduced, it relaxes the stress field of the crack tip. The crack bridging prevents the stretching of cracks; hence reduces the intensity factor of stress at the crack tip. Besides that, the toughness of the materials can be increased by plastic deformation that consumes the energy of the crack which occurs with the stretching of the crack. Fundamentally, crack bridging cell and plastic deformation toughening can be used to improve the toughness of the ceramic materials to a large extent (Rong *et al.*, 2007b).

Many researchers have reported models of cracking, for example for the $\text{Al}_2\text{O}_3 + \text{Cu} + \text{ZrO}_2$ ceramic composite material (Rong *et al.*, 2007b; Vekinis *et al.*, 1997). The ductile metal phase shows an increase solute transfer during sintering with increasing Cu content. An increase in the sintering rate and Cu content produces microstructure with a high density, thus improving the overall strength of the ceramic composite (Rong *et al.*, 2007b). Other additives such as Fe, Ti, B, Mg, Co, Ni, Mo, and Nb have been included in various concentrations to improve the sintering behaviour of the ceramic materials (Mashhadi *et al.*, 2009; Wang *et al.*, 2011; Rong *et al.*, 2007b).

The tensile stress produced by the bridging mechanism on the surface of the fracture brings several benefits. One, is to increase the extent of transformation of ZrO_2 and promote stress-induced transformation. It also extends the thickness of the stresses processed zone around the crack. The residual compressive stress caused by a mismatch of thermal expansion of ceramics and metals can also contribute to additional strength and stiffness (Zuo *et al.*, 2007). The increase in the magnitude of toughness is directly proportional to the deformation of the ductile particle. It spans the face of a propagating crack and imposes closure tractions which reduces the intensity of stress at the tip of crack (Trusty and Yeomans, 1997). The influence of the reinforcing phase is directly linked to its volume fraction and the geometrical parameters such as reinforcement size, shape, orientation and distribution (Li *et al.*, 2003).

Generally, the use of nanoparticles instead of micrometer sized particles in industrial applications has resulted in greater improvements in the physical properties (Ali and Ahmad, 2012; Hussain *et al.*, 2006). In a comparison between the two scales, nanoparticle possess a large surface area for a given volume (Zahedi *et al.*, 2015). As the surface of the particle together with its properties affect the physical and chemical interactions, a nanostructured material may possess significantly enhanced properties compared to microstructured material of a similar composition (Hussain *et al.*, 2006). Generally, for particles, fibers and plate fillers, the surface area is inversely proportionate to the diameter and thickness, respectively. Therefore, a smaller diameter or thickness results in greater surface area per unit volume (Luo and Daniel, 2003). Fig. 10 shows the shapes of common filler particle and their respective surface area-to-volume ratio. For nanofillers in the form of fibers, tubes, and layers, the ratio of surface area-to-volume is dominated by the first term of the equation. Meanwhile, the second term of the equation ($2/L$ and $4/L$) is very small and negligible. Therefore, the reduction of particle diameter, layer thickness and diameter of fibrous materials from micro to nano-scale significantly increases the ratio of surface area to volume. This phenomenon has encouraged scientists to utilize nanomaterial fillers in many composite materials (Thostenson *et al.*, 2005).

The improved mechanical properties, of hardness, wear resistance, creep resistance, and fracture strength (Barham *et al.*, 2014) of ceramics materials with nano-sized ceramic or metallic inclusions have previously been examined (Lu *et al.*, 2000; Sekino *et al.*, 1996). This system encompasses three strengthening mechanisms. The first mechanism is grain boundary strengthening effect with increased blockage of defect movement. The second improved strength mechanism of the nanocomposites is from the large reduction in the

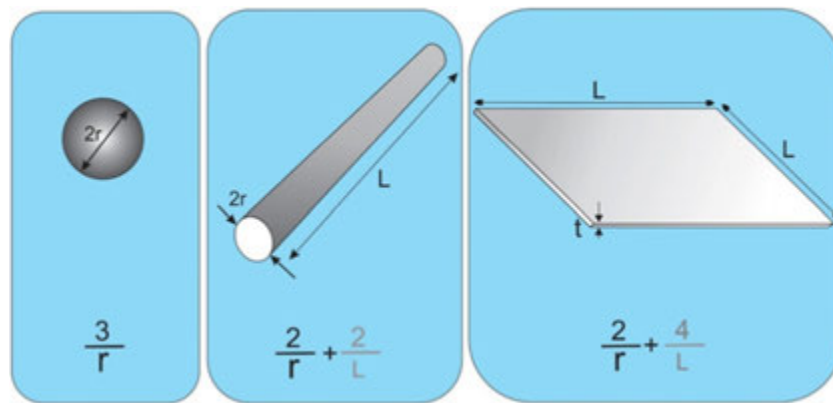


Fig. 10 Shapes of common filler particle and their particular surface area to volume ratio reprinted from. Reproduced from Thostenson, E.T., Li, C., Chou, T.-W., 2005. Nanocomposites in context. *Composites Science and Technology* 65 (3), 491–516.

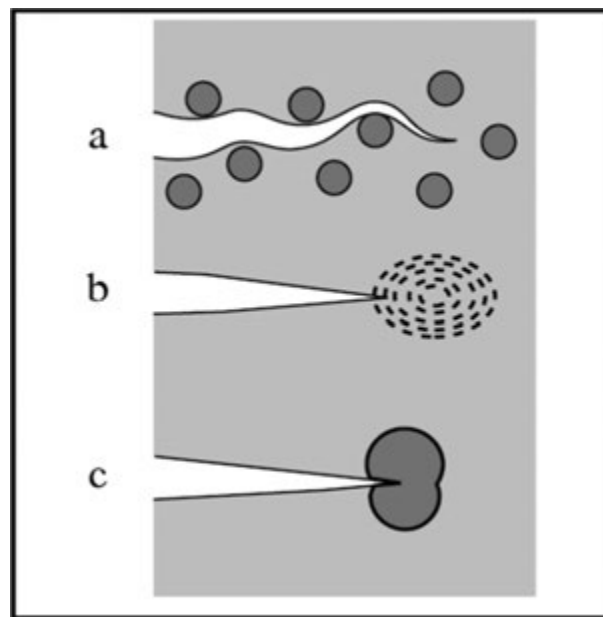


Fig. 11 Types of microstructures producing R-curve effect: a) dispersion of hard particles; b) microstructure causing multi cracking; c) phase transformation inducing compressive stresses at crack tip (case of partially stabilized zirconia). Reproduced from Boch, P., Niepce, J.-C., 2010. *Ceramic Materials: Processes, Properties, and Applications*, vol. 98. John Wiley & Sons.

size of flaws This mechanism is also linked to strengthening as a result of the formation of dislocation networks. The dislocations may form sub grain boundaries after post-annealing treatment which further improves the strength. A third mechanism linked to strengthening is the introduction of a compressive surface stress which can be achieved from an abrasive grinding operation. Although the compressive stress in the nano-composite is not relieved after post annealing treatment, the cracks produced undergo healing during the process of grinding of the surface. Thus after the annealing treatment, the strength of the nano-composite can show further improvement (Chen and Tuan, 2001; Lu *et al.*, 2000). The microstructure plays an important role on the effects of strengthening the nano-composite materials. The other factors that affect the strength of the nano-composites are intergranular site or transgranular site, size and the location of the inclusions. However, the control of the microstructure of the metal-strengthened nanocomposites is more difficult than that of the ceramic-strengthened nanocomposite (Chen and Tuan, 1999).

Much attention has been given to the increase in the behaviour of R-curve (resistance curve at cracking) (Boch and Niepce, 2010). This resistance is obtained from crack-shielding mechanisms that operate by metallic inclusions (see Fig. 11) (Bartolomé *et al.*, 2008; Sbaizero and Pezzotti, 2000). It is necessary to develop a strong ceramic/metal interface during processing in order to achieve significant toughening. When it is fulfilled, crack-bridging occurs at the ductile sites in the crack, as a result of the addition of metals. A closer stress field (e.g., bridging) can be generated from a crack extension. Generally, the magnitude of the bridging stresses is equal to the ultimate strength of the dispersed metallic particles. However, crack-bridging effect will only occur within the processed area with length that is determined by the maximum elongation-to-fracture with the inclusion of the bridge. This

means that the greater the elongation, the larger is the affected area. Thus, in ceramic polycrystal reinforced by ductile material, it is expected that toughening will be at its greatest, and its strength inclusions will be at its highest (Sbaizero *et al.*, 1998).

The microstructure of the metal-strengthened nanocomposites is more difficult to control than that of the ceramic-strengthened nano-composites. This is because metals which usually have low melting point, are usually in the molten state during sintering. Another reason is, the rate of diffusion in the liquid phase is faster than in the solid phase. Also, the wetting of molten metal is generally poor on ceramics. Therefore, the coarsening of the molten metal particles in the ceramic matrix takes place much faster than that of the solid ceramic particles in the ceramic matrix. As a result, the hot pressing method is commonly used to prepare composites reinforced by nano-technology. This technique allows the nanocomposite materials to be densified at a relatively low temperature, so as to delay the coarsening of the metallic particles. The researchers Sekino *et al.* (1996) used the hot-pressing technique to prepare Ni-strengthened Al_2O_3 . The strength of the nanocomposite can be as high as 1.6 times that of alumina alone and the size of the resulting Ni particles can be as small as 96 nm (Chen and Tuan, 1999). The properties of ceramic composite materials depend on the applied sintering method and processing conditions. In the case of Al_2O_3 -Cr nanocomposites, an increase in the ceramic phase content, is also followed by an increase in the hardness and wear resistance of the hot pressed and pressureless sintered Al_2O_3 -Cr composites. The increase in the grain size of ceramics is higher for pressureless sintering method (average grain size ~ 500 nm) than the size of ceramic grains that has undergone hot pressing method (average grain size ~ 200 nm) (Chmielewski and Pietrzak, 2007). In conclusion, the metal particles, whether in nano or microscale, play an important role in providing the toughening mechanism such as ductile particle bridging and crack deflection whereby the ductile particles enhance the mechanical properties of ceramic composite.

Conclusion

The purpose of this article was to review and highlight the effects of the addition of metal particles on mechanical properties of ceramic materials. It is generally known that ceramic materials possess excellent properties in terms of high static temperature stability, chemical stability, low bulk density, strong resistance to erosion and corrosion. However, there are limitations to the ceramic material. One of the limitation is its brittleness due to the nature of ceramic materials. One of the more significant findings presented in the research literature is that ductile metal particle can affect and improve the mechanical property of ceramic composites. When the ratio of the ductile metal particles increased in the ceramic body, the porosity has been seen to decrease, new interfacial phases have been formed, and the composite density increases. This leads to improve mechanical properties such as better bending strength, and fracture toughness, hardness and compressive strength. The metal particles, whether in nano or microscale, play an important role in providing the toughening mechanism such as ductile particle bridging and crack deflection whereby the ductile particles enhance the mechanical properties of the ceramic composite. The addition of metal particles into ceramic composite materials also play a significant role in self-lubricating property which is important in cutting tools. Another finding which is interesting to note is the effect of adding metal particles on the microstructure of ceramic composite. Increase in metal particle volume fraction reduces the grain size, which has been seen to positively affect the mechanical properties. From this review of the literature, it is evident that further research to determine the effectiveness of ductile metal particles on other properties such as electrical and the conductivity of the ceramics matrix composites should be examined.

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Static Mechanical Characterization of Ceramic Matrix Composites (CMCs)

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Introduction

Ceramic matrix composites (CMC) are a subset of composite materials and a subset of technical ceramics. Major group of CMCs considers ceramic fibers embedded in a ceramic matrix, thereby forming ceramic fiber reinforced ceramics (CFRC). Both the matrix and the fibers can consist of any ceramic material, whereby carbon and carbon fibers can also be considered ceramics (Chung, 2017a; Davim, 2016; Cooke, 1991).

Development of ceramic matrix composites has led to overcoming the existing problems of technical ceramics (alumina, zircon, silicon carbide, silicon nitride, aluminum nitride etc.), such as fast fracture under mechanical or thermo-mechanical loads resulting from small external or internal defects (pores or scratches) (Chung, 2017b). Ceramics, as well as glass, are very susceptible to these types of defects. At first, in order to increase fracture toughness, technical ceramics were being added secondary phases to act as barriers against crack propagation. Particles (whiskers) of the added phase were often made up of other ceramic materials and with a much finer grain. Their task was to stop the crack from propagating further, once it had reached them (Mukerji, 1993). This type of reinforcement had its limitations and such CMC materials found use only in some tool ceramics (Peters, 1998). Introducing secondary fibers into 2D or 3D ceramic matrix significantly increases fracture toughness, elongation and resistance to thermal shocks, while maintaining high strength and Young's modulus of elasticity of the ceramic matrix. The fibers are often chosen to have a somewhat higher Young's modulus than the Young's modulus of the matrix itself (Belitskus, 1993).

Fiber reinforcement increases toughness of the ceramic matrix in multiple ways. First, a crack propagating through the matrix comes across a fiber and is, therefore, made to propagate around it in order to continue the fracture process. Further, the weak bonding between the matrix and fibers allows fibers to begin pull out from the matrix. Both processes consume energy, increasing the fracture toughness. Ultimately, unbroken fibers can stop any further crack propagation (Basutkar and Kolekar, 2015). Functional role of these fibers is to ensure an increase in required stress for the propagation of microcracks through the matrix, which usually takes place along the grain boundary, therefore increasing the energy consumption of the crack propagation. Once the crack appears and starts spreading due to an increase in limit stress, the fibers are supposed to bridge the crack without fracture, consequently giving the CMC high resulting tensile strength (Fig. 1). On one hand, composite initial resistance to crack propagation is increased in this way and, on the other hand, sudden brittle fracture characteristic for monolithic ceramics is avoided. This behavior differs from the behavior of ceramic fibers in composite materials with a polymer or a metal matrix, where the fiber breaks before the matrix, since polymers and metals have significantly higher plasticity than the ceramic materials. Unlike polymer and metal composite matrices, ceramic composites require weaker bonding between the matrix and fibers. This is achieved by precipitating a thin layer on the fibers (e.g., pyrolytic carbon or boron nitride), which weakens the fiber/matrix interfacial bond that further lead to the fiber extraction on the crack surface. Thus, fiber/matrix interfacial structure control is very important for CMC (Kodgire and Kodgire, 2018).

In CMCs, most often used materials both for the matrix and for the fibers are: carbon (C), silicon carbide (SiC), alumina (Al_2O_3) and mullite ($\text{Al}_2\text{O}_3\text{-SiO}_2$) (Bansal, 2005).

Ceramic fibers in CMCs can have polycrystalline structure, as in conventional ceramics. They can also be amorphous or have non-homogenous chemical composition that develops after the pyrolysis of organic precursors. High process temperatures required for making CMC exclude the use of organic, metal or glass fibers (Jones, 2001). Only the fibers stable at temperatures above 1000°C can be used, such as alumina, mullite, SiC, zirconium or carbon fibers. Amorphous SiC fibers have the ability to elongate more than 2% - much higher than conventional ceramic materials (0.05% to 0.10%) (Cooke, 1991). The reason for this SiC fiber property is the presence of additional elements in them, such as oxygen, titanium and/or aluminum, which give higher tensile strength. These increased elastic properties are especially convenient in various three-dimensional fiber arrangements where the bend radius is small (Kumagawa *et al.*, 1998).

Important commercially available CMCs are C/C, C/SiC, SiC/SiC i $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ (fiber material/matrix material).

Typical properties of long fiber ceramic composites are: high mechanical strength even at high temperatures, high thermal shock resistance, high stiffness, high toughness, high thermal stability, low density and high corrosion resistance even at high temperatures, anisotropic properties that accompany fiber orientation and improved properties of fatigue behavior.

Characterization of Ceramic Composite Materials

The tests aim to determine the properties of the material in conditions similar to working conditions. In order to use the materials as purposefully as possible for the appropriate needs, not only from the technical but also from the economical point of view, a comprehensive knowledge of their chemical, physical, mechanical, technological and exploitation properties is required (Czichos *et al.*, 2006).

Chemical properties are determined by qualitative and quantitative chemical analysis, whereby the composition of the material and the weight share of individual ingredients are determined. In most cases chemical analysis does not provide sufficient data on

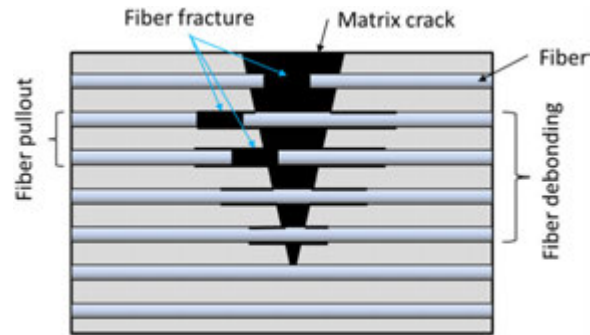


Fig. 1 Scheme of the crack bridges at the crack tip of ceramic composites.

material quality, which is why physical and mechanical tests are done in addition. The task of physical tests is grasping the physical properties of the material, especially thermal, electrical and magnetic, and also specific weight, external appearance, and other. Mechanical properties of materials (like different types of strength, hardness, toughness) have the highest influence on the choice of materials for majority of technical purposes, which is why mechanical tests are considered the most important ones and often performed in a series of tests (Vitez *et al.*, 2006).

According to the way the force acts, all mechanical tests can be divided into static and dynamic. Static tests are the most common and are performed under a constant load or a slowly increasing load. Dynamic tests use loads that change over time according to a certain law or impact loads.

According to the temperatures at which the tests are performed they can be divided into: ambient temperature tests, elevated temperature tests and reduced temperature tests. The tests are most often performed at ambient temperatures, i.e. room temperature. Tests at reduced and elevated temperatures are performed in special cases, when the influence of temperature on the material properties needs to be determined. According to the applied loads or the size of the observed sample - tests can be performed at a macro, micro or nano scale.

Tests are also categorized as standard and non-standard. Standard tests are based on predetermined regulations (standards), both in terms of the test procedure and in terms of the devices and samples used, respecting the certain specifics of the material that is being tested. Non-standard tests are mainly performed when there are no standards for individual tests (Jenkins *et al.*, 2000). In the case of ceramic coatings, different scratch test methods can be used for their characterization (Zivic *et al.*, 2012), or tribological test in relation to wear and friction (Mitrovic *et al.*, 2016). New methods for characterization of composites have been studied (Pluta *et al.*, 2021), as well as methods of analysis, like analysis of statistical data related to static fatigue or tensile properties (Mazerat and Pailler, 2020) or analysis of mechanical properties for ballistic ceramic (Dresch *et al.*, 2020). Measurement methods of friction coefficient between CFRP laminate layers have been studied (Saito and Kimpara, 2010).

Test samples can be standard and non-standard. Standard samples have precisely defined dimensions and are shaped for testing. On the other hand, non-standard samples are usually raw materials and finished products that are subjected to certain tests. The sampling process should ensure that the representativeness of the tested material and the method of sample preparation do not change the characteristics of the material. Collecting, producing and preparing the samples are very important phases that precede the test itself. Choosing a representative sample is often more important than the accuracy of the method. In an effort to obtain a representative sample, the following must be taken into account: choosing the sampling location, sample amount, sampling frequency, methods and ways of cutting and shaping. Samples can be cut from prepared semi-finished products and components or can be made separately (Kaufmann, 2003; Hodgkinson, 2000).

In the case of non-compact materials that consist of several different phases, as is the case of composite materials, it is necessary to take into account the appropriate representation of phases (matrix, reinforcement), as well as their position in the material in relation to each other. These materials have completely different properties from their constituents and also behave differently. In that case, it is most purposeful to know the properties of the constituents, as well as the properties of the material as a whole. In some cases, like fiber reinforced ceramic matrix composites (CMCs), it is also important to know the characteristics of the fiber/matrix interface (Carlsson, 2013).

Testing of the composite materials has three main general objectives (Daniel and Ishai, 2006):

- (1) Determination of the basic properties of unidirectional composites, which is the basis for design and analysis;
- (2) Research and verification of the analytical predictions of mechanical behavior;
- (3) Independent experimental study of material behavior for certain geometries and load conditions.

These general objectives include the following:

- (1) characterization of the constituent components of the CMCs: fibers, matrices and interfaces (knowing their properties can predict the behavior of the composite itself and the behavior of the system),
- (2) characterization of the elementary unidirectional pattern that represents the structural unit of the composite,
- (3) determination of interlaminar properties,

- (4) behavior of the material under special load conditions (e.g., multiaxial, fatigue, creep, impact, etc.),
- (5) experimental analysis of stresses and damage of the composite constituents and composite structure, especially those involving geometric discontinuities.

Various experimental methods are used for the aforementioned applications. Most of them measure deformations or stresses. Experimental methods for composite materials are more complex than experimental methods for isotropic materials and often require significant modification (Friedrich, 1989).

Mechanical Tests

The mechanical characteristics that determine the material quality can be very different and there are a large number of them. This means that there are many procedures for their testing and the result interpretation must be done carefully with respect for all the specifics of individual cases.

The mechanical resistance of a material is determined by its mechanical properties. Mechanical properties are very important because they are the basis for design and dimensioning of machine components and elements. When dimensioning, it is necessary to consider the intensity, types and duration of all possible mechanical loads that will occur during exploitation. Therefore, machine components or system elements are dimensioned based on those mechanical properties that characterize the mechanical resistance of the material for certain operating conditions. The main objective is to prevent fracture or plastic (permanent) deformation during exploitation, which would functionally disable further operation of the machine part or the entire system.

According to the mode of force action, mechanical testing is divided into two groups: static testing and dynamic testing.

Characteristic of the first group of tests is that there are no shocks or vibrations of the sample during testing, because the force acts uniformly. However, in the second group of tests, the force intensity changes in a unit of time, and as a result of that - the samples are exposed to dynamic shocks and vibrations during the testing.

Although mechanical testing procedures for monolithic materials, including ceramics, have been well developed and standardized over the years, testing of fiber reinforced materials generally requires modification of the existing methods or development of new methods (Carter and Norton, 2007). Polymer matrix composite (PMC) technology is older than ceramic matrix composite (CMC) technology, and the current development of mechanical CMC testing relies heavily on the polymer matrix composites testing. However, as the requirements for composites differ from the requirements for monolithic materials, the requirements for testing different types of composites also differ (Anand and Dutta, 2013).

Mechanical testing of composite structures in order to obtain parameters is a time-consuming and often difficult process. However, this is an essential process and it can be somewhat simplified by testing simple structures, like straight-sided samples. The data obtained by this type of testing can then be directly related to varying degrees of simplification and accuracy with any structural form. The testing methods listed here represent only a short selection of methods available to composite focused professionals. Some tests, such as the tensile tests, compression tests, etc. are standardized, while there are number of tests for determining the properties of materials that are not yet standardized.

Static Testing

During static testing, materials are exposed to relatively calm ("static") loads, both at room temperature and at elevated and reduced temperatures. In reality, these loads are not completely static, but the rate at which their intensity changes over time is small, so they are considered as static. According to the type of stresses that occur in the material, static tests are grouped as: tensile, compression, bending, twisting, and shear tests. In the first three cases, external forces in the observed cross section cause normal stresses, while in the last two shearing occurs.

The mechanical properties of ceramic composite materials, as well as their constituent components (matrices and reinforcing fibers) are mainly determined in order to assess their properties because characteristics of the finished product will largely depend on those properties. Mechanical properties are usually determined by applying tension, compression, bending and shearing (Daniel and Ishai, 2006). The test samples are shaped, as much as possible, according to the standards and guidelines provided for the selected test procedure. The samples can have circular or rectangular cross-section, and can be made separately or cut from already existing components. Since CMC materials are usually hydrophilic due to the presence of open pores, it is necessary to carefully prepare the samples, as well as to control the laboratory environment, before and during the testing. Since ceramics are sensitive to the rate of deformation, test speeds have to be well defined (Carlsson *et al.*, 2000).

Tensile Testing

Tensile testing of the material sample at room, elevated and reduced temperatures is the most characteristic test in the group of static tests and most often performed. It aims to determine the resistance and deformability properties, namely: yield strength, tensile strength, elongation and contraction, as well as the modulus of elasticity.

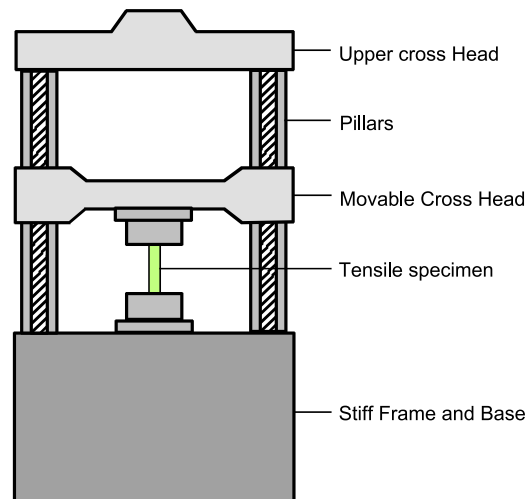


Fig. 2 Universal testing machine.

The test procedure consists of exposing a sample made of the test material to a tensile force that is slightly increasing from zero to a maximum value, when the test sample usually fracture. During this process, the material sample gets deformed (elongated and contracted). Therefore, the tensile test aims to determine the behavior of the material under a uniaxial tensile load that is evenly distributed across the cross section of the test sample.

This testing method is described in the standard ASTM C 1275 and it can be used for material development, material comparison, quality assurance, characterization, and providing data needed for part design. The tensile strength of a ceramic material depends not only on the properties of the material, but also on the presence of various defects (internal and external defects of the material that can be detected by analysing the surface or the fracture). The test environment (vacuum, gas, ambient air, etc.) including moisture content can have a significant effect on the measured strength. If the test conditions are different from those prescribed in regulations, these differences have to be pointed out in the test report. During the preparation of the test sample surface, defects can be introduced (damage caused by processing) which can have pronounced effects on the test results (increased frequency of surface-initiated fractures). Surface preparation can also introduce residual stresses, so their values should be minimized.

The device on which the tests are performed is usually an universal testing machine (UTM, tensometer) ([Fig. 2](#)) which must comply with the regulations given by the standards. Each UTM must have defined and verified accuracy. Since ceramics are very hard materials and have problems related to the sample slipping and damage, it is necessary for the UTMs to have appropriate clamping jaws that will prevent sample slipping and damage. Clamping jaws, depending on the way they provide tightening, can be active or passive ([Freiman and Mecholsky, 2012](#)). Active clamping jaws transmit mechanical, hydraulic or pneumatic tightening of the test sample ([Fig. 3a](#)), whereas passive clamping jaws transmit the load via a direct mechanical connection, which is achieved through the geometric characteristics of the sample ([Fig. 3b](#)).

Testing machines need to have analog and/or digital option of collecting and storing data on the tested values (load, stress as a function of time, displacement or deformation) ([Carlsson et al., 2000](#)). A digital record makes the data analysis easier. Force-elongation and stress-strain are commonly drawn diagrams. Micrometers and other linear measuring instruments should be accurate and precise.

Test samples can be cylindrical or prismatic (straight-sided). Cylindrical samples are made from bar-shaped materials and their production is relatively simple. Quality of the final processing must be taken into consideration, as well as dimensional and shape tolerances of the sample ([Hodgkinson, 2000](#)). Straight-sided samples are mostly made from plates or blocks and are easy to make ([Carlsson et al., 2000](#)). Regardless of whether it is a cylindrical ([Fig. 4a](#)) or prismatic sample ([Fig. 4b](#)), it mainly consists of a wider and a narrower part. The narrower part is the measuring part of the sample and it is expected to break, while the wider extensions at the ends have the task of facilitating the tightening of the sample in the clamping jaws and preventing it from slipping during a tensile test ([Daniel and Ishai, 2006](#)). The extensions can be flat, stepped or conical, or with holes drilled into them to insert a safety fuse in the form of a pin to prevent slipping ([Fig. 5](#)). The surfaces of the clamping jaws, which are in contact with the test samples, must ensure that the test sample does not slip, which is achieved by increasing the clamping force and the coefficient of friction between the sample and the jaws ([Jenkins et al., 2000](#)). Increasing the tightening force can lead to crushing of a part of the sample in the jaws, which is not allowed. On the other hand, the increase in friction can be provided by machining notches on the surfaces. An alternative may be to apply a coating of tungsten carbide particles with thermal spraying. Another approach would be to modify that surface by some processing, like shot peening ([Mitrovic et al., 2014](#)).

It is also possible to prevent the sample from slipping by drilling a hole in the extended part and placing a pin that would provide a firm connection between the sample and the jaws. This solution is mostly avoided because of the stress concentration created due to the drilled hole and the possible fracture of the sample at that point. One of the possible ways to increase the friction is to glue the tabs on both sides at both ends of the sample, as shown in [Fig. 4c](#). The material of these tabs is different from the tested material and it is most often some polymer composite, aluminum or brass ([Jenkins and Zawada, 2000](#)). The adhesive

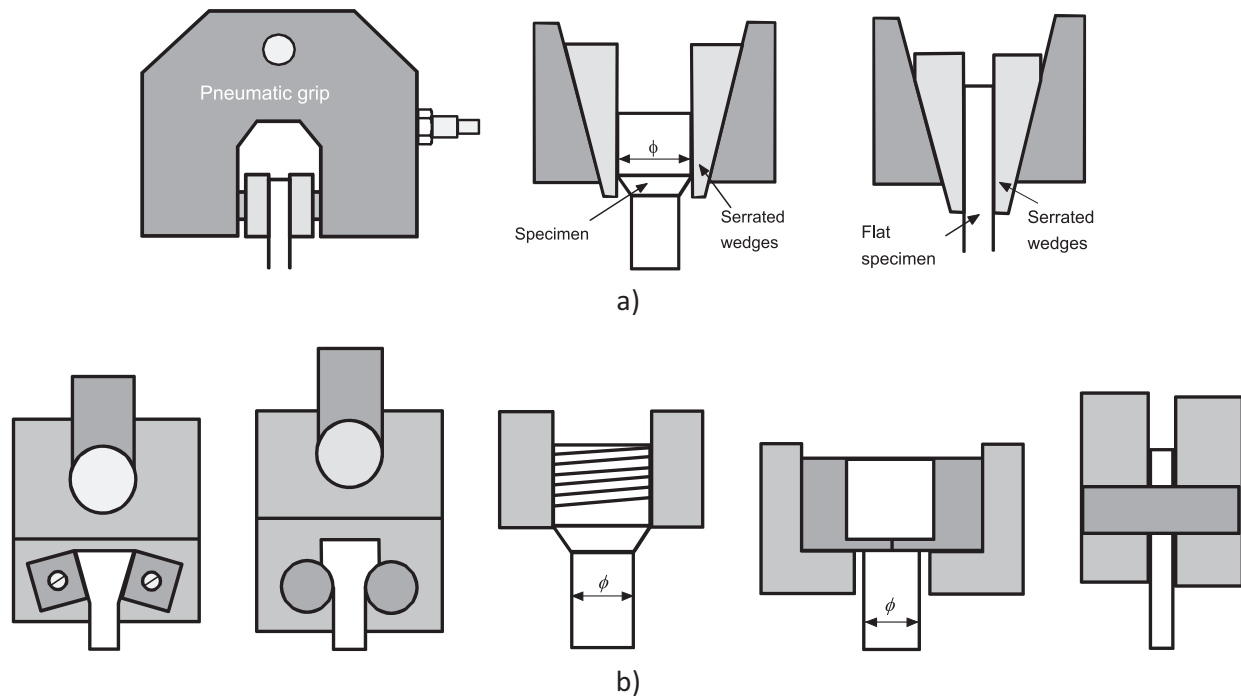


Fig. 3 Active (a) and passive (b) clamping jaws.

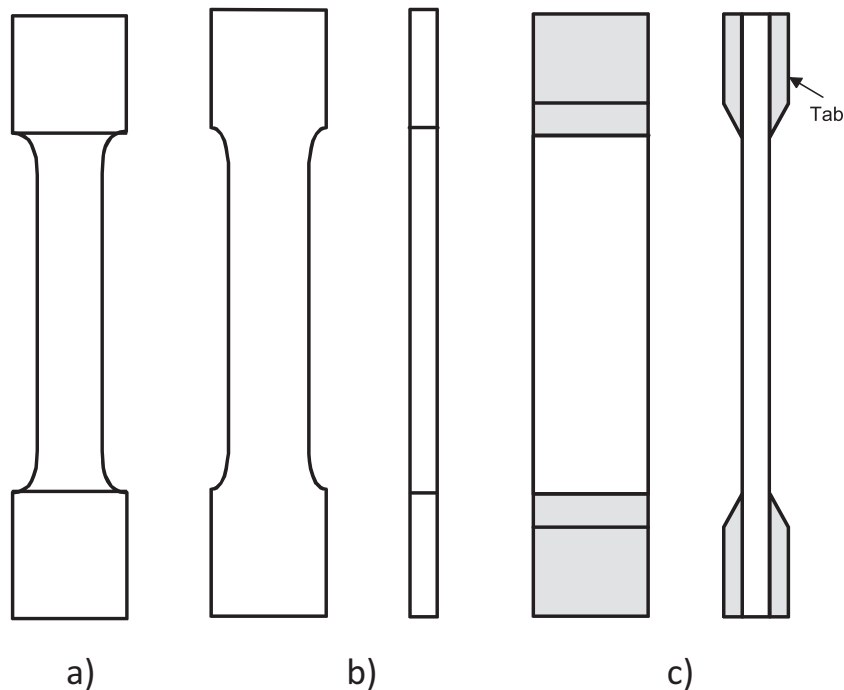


Fig. 4 Layout of the tensile test sample: (a) Cylindrical specimen, (b) Untabbed, dog-boned flat specimen, (c) Tabbed, straight-sided flat specimen.

used to glue the tabs to the sample should have sufficient strength to prevent shearing at the place of gluing before the destruction of the sample itself (Hodgkinson, 2000).

During the testing, it is necessary to ensure the parallelism of the tensile load. The test speed should be such as to ensure the obtaining of the maximum tensile strength. It is considered that the stress gain during the test should be from 35 to 50 MPa/s, and

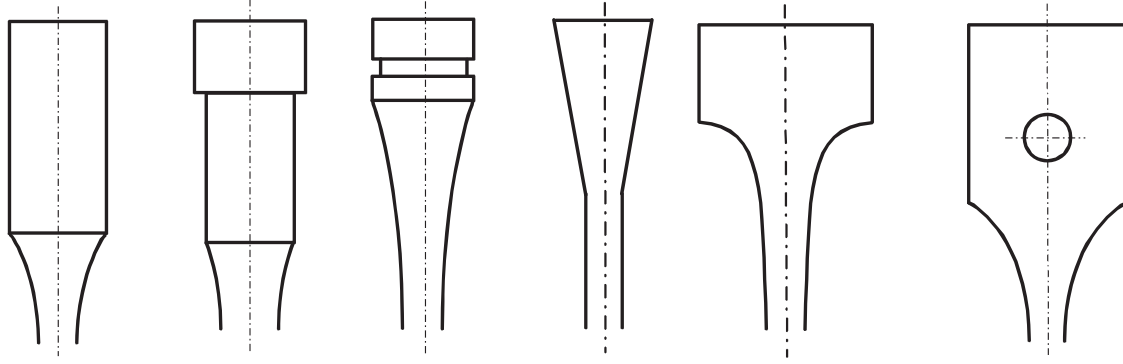


Fig. 5 Shapes of the tensile test sample extensions.

that the whole test should be done in 5–10 s. It is recommended that the speed of the moving clamping jaw be 1–2 mm/min (Hodgkinson, 2000).

The total number of tested samples has a very important role in estimating the exact values of the characteristics that are being determined. The increased number of samples increases the accuracy but it also increases the cost of testing. It is acceptable to perform the test on at least 5 samples, and if there is a need (large scatter of results, importance of results, etc.) then the test can be performed on a higher number of samples.

If it is necessary to determine the modulus of elasticity, then the testing machine has to be equipped with a suitable extensometer for measuring small deformations or strain gauges. An extensometer should be used carefully, so not to damage the sample surface with its sharp edges. Usually, the surfaces of the sample are smooth and shiny, and the edges of the extensometer blade can slip, so it is necessary to use an agent at the point of contact between the extensometer and the sample, which will increase friction and thus prevent slipping (Hodgkinson, 2000). Development of suitable strain gauges is not an easy task (Khoshgoftar and Abbaszadeh, 2020).

To measure the Poisson's ratio, it is necessary to use two strain gauges for biaxial measurement ($0^\circ/90^\circ$ rosette) or a biaxial extensometer for measuring longitudinal and transverse deformations at the same time. There are different techniques to measure the Poisson's ratio (De Baere *et al.*, 2007).

After the fracture of the examined sample, a fractographic examination of the fracture would be desirable in order to determine the cause of the fracture (especially in those samples where there is a significant deviation of strength from the average values). Porosity, inclusions, agglomerates and random large grains within the material can affect the fracture of the sample, and in the case of surface samples, these are most often cuts caused by mechanical processing or accidental mechanical damage.

The tensile strength R_m is calculated by the formula:

$$R_m = \frac{F_{max}}{S_0}, MPa$$

where: F_{max} - maximum force (load required to break the sample) [N], S_0 - initial area of the measuring part of the test sample [mm^2].

Young's modulus of elasticity E represents the ratio between stress σ and strain ε (provided that stress and strain are measured in the range of proportionality – a linear relationship between stress and strain). It is determined by the formula:

$$E = \frac{\sigma}{\varepsilon}$$

where σ is the technical stress which is determined by the following equation:

$$\sigma = \frac{F}{S_0}, MPa$$

where F is the applied load in N, and S_0 is the cross-sectional area of the tested sample in mm^2 .

The technical strain ε is determined by the formula:

$$\varepsilon = \frac{(l - l_0)}{l_0}$$

where: l_0 - initial length of the extensometer in mm, l - length between the feeler arms of the extensometer at any time (in the area of proportionality) in mm.

Fracture deformation is determined by the formula:

$$\varepsilon_f = \frac{(l_f - l_0)}{l_0}$$

where: l_f - length of the sample at fracture in mm, l_0 - initial length of the sample in mm.

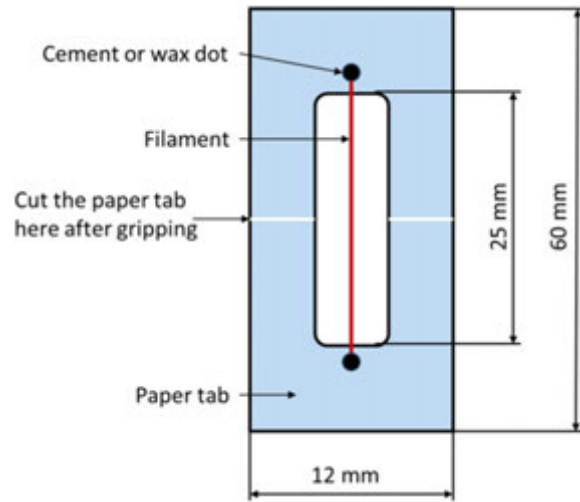


Fig. 6 Setup for the single-fiber test ASTM D3379 (Sample with one fiber).

Tensile Testing of Reinforcement Fibers

Tests for examination of the fibers are used for the purpose of quality control and assessment of the effects of potentially harmful treatments of their surfaces. They are also used to assess the degradation of fibers in the environment and to determine the mechanical properties required for micromechanical analyzes (Rauch *et al.*, 1968). Most fiber testing methods are designed to determine the modulus and strength of fibers under uniaxial tension, although other tests also exist (Daniel and Ishai, 2006).

The single-fiber test (ASTM D3379) prescribes a procedure for determining the modulus of elasticity and tensile strength of fibers. For this test, one fiber is separated without damage and placed on the cardboard while centering and gently tightening it over the opening, as shown in Fig. 6. The ends of the fiber are glued to the cardboard and then the sample together with the cardboard support is placed on the testing machine, after which the sides of the opening are cut on both sides of the fiber (Ntenga *et al.*, 2019). After that, the fiber is stretched until it breaks. The stretched fibers usually show a linear elastic behavior until the fracture (Carlsson *et al.*, 2014). For the test to be successful, it is necessary to provide a testing machine with a tensile force of 5–20 N (0.5–2 kg). There is usually a large scattering of results (mainly due to uneven fiber diameters), which is why it is necessary to test a large number of samples in order to obtain reliable results (Ilankeeran *et al.*, 2012; Veliky, 2015). The determined values (strength and modulus of elasticity) will be greatly influenced by the accuracy of fiber diameter measurements, which is why it should be performed with great care (Park and Seo, 2011).

The modulus of elasticity of the fiber is defined as follows:

$$E = \frac{\sigma}{\epsilon}$$

where σ is the fiber stress that is determined by the following equation:

$$\sigma = \frac{F}{S_f}, \text{MPa}$$

where F is the applied load and S_f is the cross-sectional area of the fiber.

Deformation ϵ is determined as the ratio between the displacement of the clamping jaws δ and the initial fiber length between the jaws l_{f0} :

$$\epsilon = \frac{\delta}{l_{f0}}$$

The tensile strength of the fiber is determined as the ratio of the force at the moment of the fiber fracture F_{max} and the initial cross-sectional area of the fiber S_{f0} :

$$R_m = \frac{F_{max}}{S_{f0}}$$

Compression Tests

Testing of ceramic matrix materials or CMCS is performed for research, development and quality control. Compressive properties include modulus of elasticity, compressive yield strength, and compressive strength. In general, ceramic materials and CMCS have higher resistance to pressure than to tension. Ideally, ceramics and ceramic composites should be under pressure during use, although in practice they are often subjected to tension. However, the pressure behavior of these materials is very important.

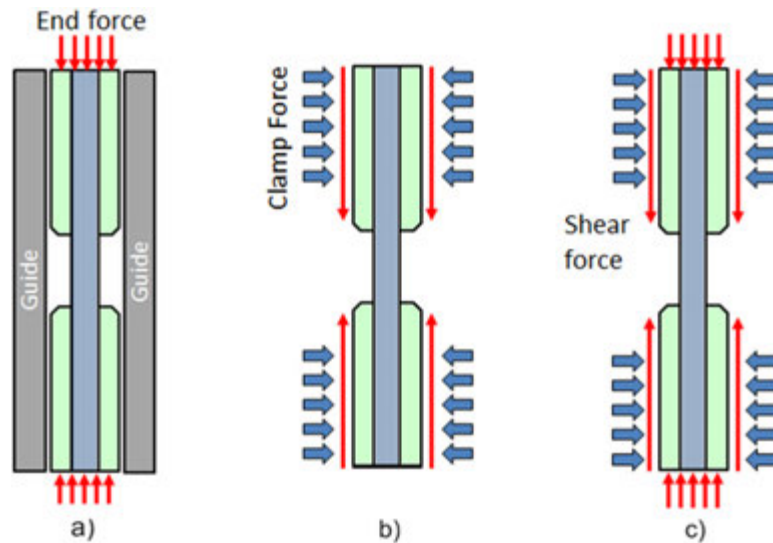


Fig. 7 The ways of achieving compressive loads: (a) loading the front side of the sample, (b) shear loading (using clamping jaws), (c) a combination of the previous two cases.

Compression tests provide information on the strength and deformation of the materials under a monotonic uniaxial compressive load. The results of these tests are needed to evaluate the material behavior in the occurrence of various cumulative damage processes, such as, for example: matrix cracking, matrix separating from fibers, fiber cracking, delamination, etc. (Carlsson *et al.*, 2014). The obtained results of compression tests can largely depend on the environmental conditions and the way of testing (temperature, humidity, test speed, etc.), which is why special attention should be paid to these conditions. Preparation of test samples is also very important. Damage caused by processing or high residual stresses due to processing can affect the accuracy of the obtained test results. During compression the sample may bend, which leads to geometric instability of the sample and uneven load acting on the fibers. Fractures that occur outside the measuring part (uniformly stressed area) can be a consequence of stress concentration due to geometric transitions or external stresses introduced by clamping jaws. Samples destroyed in that way must be rejected as invalid. In addition, the friction caused by the contact between the sample and the clamping jaws plays a very important role during testing. If the friction is low, then the clamping force should be high, which can lead to local crushing of the sample (Park and Seo, 2011). In contrast, with low friction, if the clamping force is small, the outer layers may shear and the sample may slip in the jaws. Side supports are sometimes used in compression testing to reduce sample protrusion. However, these side supports can lead to friction, which would artificially increase the load required to break the sample. In addition, side supports and increased friction could invalidate the assumption of the uniaxial stress state. Therefore, when using side supports, the friction effect should be quantified and its impact reduced to a minimum (Daniel and Ishai, 2006).

The compression test can be performed on universal machines or other devices that can achieve a monotonous uniaxial load, with the appropriate registering of the force and deformation (shortening) during the testing. Loading can be electromechanically, hydraulically or pneumatically applied. The transfer of uniaxial load from the machine to the test sample is performed by compression plates, clamping jaws or a combination of compression plates and clamping jaws (Fig. 7). If the compression testing is performed from the front sides (by compression plates) then the ends of the sample have to be parallel and orthogonal to each other in relation to the sample axis (Hodgkinson, 2000).

Clamping jaws are usually made from serrated hardened steel, with or without hard coatings. These thermal spray coatings, which consist of hard tungsten particles in a cobalt or nickel matrix, are relatively smooth and gentle, so their removal and repositioning usually represent a significant cost. These surfaces, although smooth, have an equal or better holding power than the serrated surfaces.

The biggest problem with compression testing is that the sample buckles before fracture. This problem is usually easily solved by reducing the sample length or providing appropriate side support. The applied constraints often do not represent the actual loading conditions during the exploitation of the material (Carlsson *et al.*, 2000).

There are several types of compression tests for composite materials. Some of these methods are standardized by the company, national or international standards, while others are not standardized at all. Some of the most important methods will be shown here. The compression test samples are generally short and have sufficiently large cross-sections to reduce the possibility of buckling. The cross-section is usually circular, square, rectangular or a ring if the sample is a pipe. However, since most composites are available in the form of thin plates, from which straight-sided samples are made, it is necessary to prevent the sample from buckling with an appropriate side support.

Clamping jaws (and/or compression plates) are an integral part of the testing machine that connect the test sample to the machine and transfer the load from the machine to the sample. Load transfer can be achieved with an active or a passive contact.

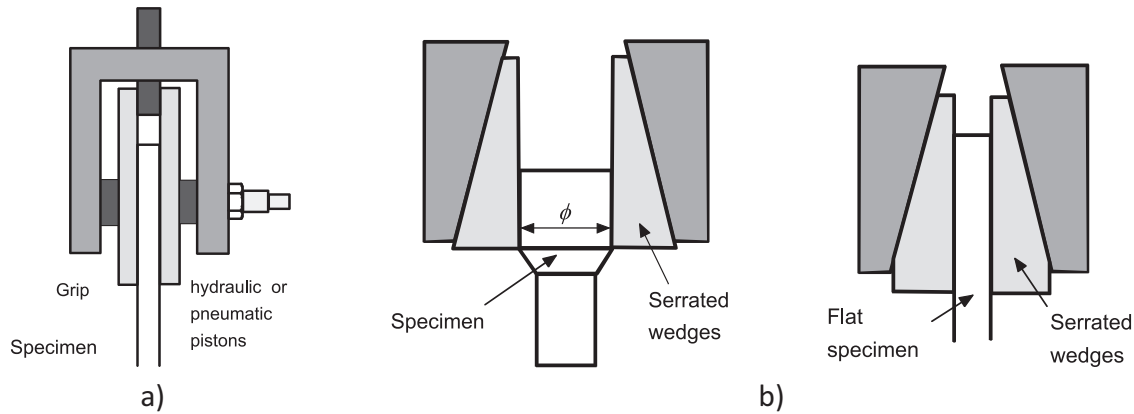


Fig. 8 Active clamping jaws: (a) pneumatic or hydraulic, (b) mechanical used for circular and prismatic samples.

An active contact requires a continuous application of mechanical, pneumatic or hydraulic load transfer systems during the test (Wegner and Adams, 2000). The transfer of uniaxial load from the machine to the sample is achieved through friction between the held part of the sample material and the jaws of the machine. Normal force acting on the sample is achieved by mechanical, pneumatic or hydraulic means (Fig. 8). Uniform pressure and a constant coefficient of friction are required in order to achieve uniform contact (Hodgkinson, 2000).

In addition to active clamping jaws, there are also passive ones (compression plates). They, unlike active jaws, do not use friction, but directly lean on the test sample and transfer the load from the machine. When compression testing CMCs, due to the very brittle ceramic matrix, it is necessary to ensure good surface contact between the sample and the compression plates. Point or line contacts and uneven pressure can produce Hertzian contact stress that can lead to cracks and fractures. Therefore, it is necessary for the front surfaces to be flat and parallel within the given tolerances.

Regardless of whether it is an active or a passive clamping (compression) device, it has to provide a uniaxial load without subsequent bending (buckling) of the sample.

Deformation during compression testing can be measured with an extensometer or with strain gauges (Staab, 2015). If a mechanical extensometer is used then damage to the sample surface can occur due to their contact, which must be prevented. The weight of the extensometer should also be taken into account, so that bending is not greater than the allowed. If there is a danger of the sample buckling, it is necessary to register the lateral movement of the tested sample.

Test data can be obtained in analog or digital form, depending on the type of test machine. Digital data is more favorable because of the possibility of latter analysis. It would also be of interest to register the compression diagram which gives the connection between the compressing force and the shortening of the sample, i.e., the stress and deformation.

There are recommended shapes for pressure test samples, although any other geometry is acceptable if certain requirements are met regarding the sample tightening, the fracture site, and the allowed bending of the sample. If there are geometric transitions on the sample, there will always be a bigger or smaller concentration of stress in those areas, which can significantly reduce the compressive strength.

The test samples can be completely straight-sided as shown in Fig. 9. Such samples can be used for various types of compression contacts. If the compression is performed from the front sides, those surfaces have to lie within the tolerances (parallelism and alignment). In this case, there is a greater possibility of the sample buckling, so it may be necessary to secure the sides from buckling. The hatched part of the sample is placed in the jaw of the machine while the middle part is free and exposed to compression. The middle part is significantly shorter than the end parts in order to avoid buckling.

Standard ASTM C 1358 recommends that compression test samples have shapes as shown in Fig. 9. Samples can be straight-sided (Fig. 9a) or with an extended conical end, so-called "Bow-Tie" (Fig. 9b). If the samples are straight-sided, the central part of the sample should be ~25 mm long, while the end parts are at least 50 mm long, with the width of at least 10 mm and thickness of at least 3 mm (Fig. 9a). For the samples with conical ends, the length of the central part is 30.5 mm and the width is 12.7 mm. The length of the conical parts is 22.9 mm, and the thickness is 3 mm or more. However, it is possible to use other combinations of dimensions, as long as the slenderness ratio is complied with: $\frac{l}{b} \leq 5\sqrt{3}$, where l is the length of the middle measuring part of the sample and b is the sample thickness.

To prevent damage to the sample when tightening the jaws, it is possible to stick appropriate plates (tabs) on both sides of the ends of the sample (Fig. 10). Tabs can be made from different materials (polymers, composites, metals, etc.) and are glued with a suitable adhesive that should provide a sufficiently strong joint that would not break during testing (Chatterjee et al., 1993a,b). Tabs are most often made out of fiber-glass reinforced epoxy, polymethylene resins (PMR), or carbon fiber-reinforced resins as well as aluminum [ASTM C 1358]. It is recommended to choose a material with a similar modulus of elasticity as CMC (Hodgkinson, 2000). Tabs should be at least 50 mm long and the same width as the sample. Samples are made by cutting and fine processing to the specified dimensions. Testing requires at least 5 samples. If there is a large scatter of results then testing should be performed

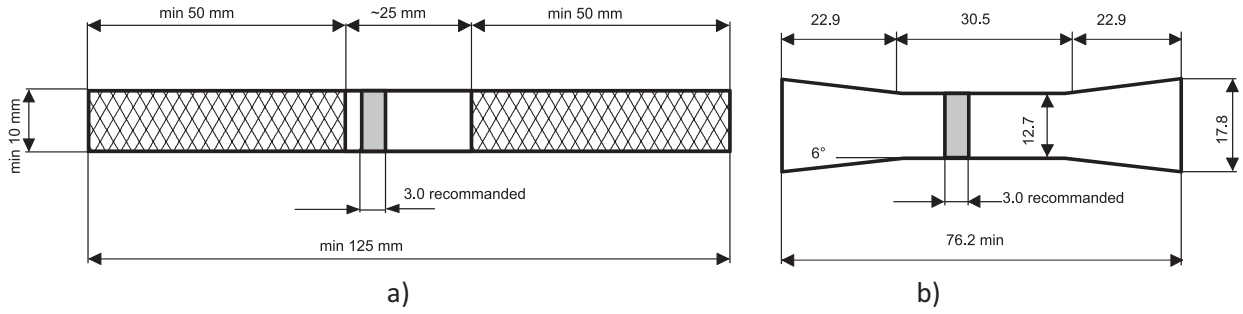


Fig. 9 Examples of compression test specimens (a) Straight-Sided, (b) "Bow-Tie".

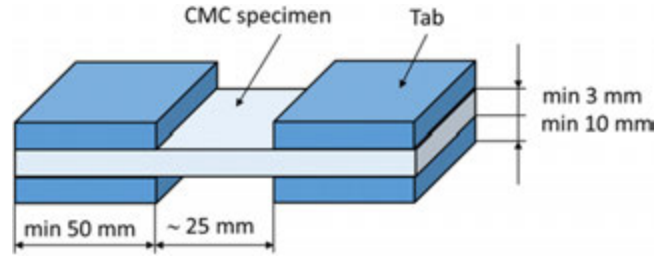


Fig. 10 Sample of the compression test material with tabs.

on a larger number of samples, although this makes the testing more expensive. If the available material and its price limit the number of samples, testing is possible on a smaller number of samples.

The test speed should be selected in such way to allow test duration of 5–7 s, from the start until the fracture.

Based on the performed tests, the compressive strength R_{cm} can be calculated according to the following equation:

$$R_{cm} = \frac{F_{max}}{S_0}, \text{ MPa}$$

Where: F_{max} - maximum force required to break the sample, N, S_0 - initial cross-sectional area of the test sample, mm^2 .

Since CMCs are brittle materials, they break at the moment of reaching the maximum force, so the compressive and fracture strength will have the same values.

The shortening of the sample at fracture is determined by the following equation:

$$A_c = \frac{(l_0 - l_f)}{l_0}, -$$

Where l_0 is the initial length (measuring length) of the tested sample in mm, and l_f is the length of the sample at the moment of fracture in mm.

The modulus of elasticity is calculated as:

$$E = \frac{\Delta\sigma}{\Delta\varepsilon}$$

Where $\Delta\sigma/\Delta\varepsilon$ is the slope of the curve on the compression diagram ($\sigma - \varepsilon$ diagram).

If longitudinal (ε_L) and transverse deformation (ε_T) of the sample are measured during the test (usually using a strain gauge rosette $0^\circ/90^\circ$) then the Poisson's ratio (ν) can be calculated using the equation:

$$\nu = \frac{\Delta\varepsilon_T}{\Delta\varepsilon_L}$$

where the ratio $\Delta\varepsilon_T/\Delta\varepsilon_L$ represents the slope of the linear part of the $\varepsilon_T - \varepsilon_L$ diagram.

The stress value at the compressive yield strength can be determined in the same way as when compressing metal materials.

For each series of tests, test results are usually statistically analysed to determine average values, standard deviation and coefficient of variation.

Bend Testing

Bend testing does not provide a pure stress state, because the material is simultaneously stretched, compressed and sheared, therefore this test does not serve to determine the basic properties of ceramic composite materials. However, bend testing is

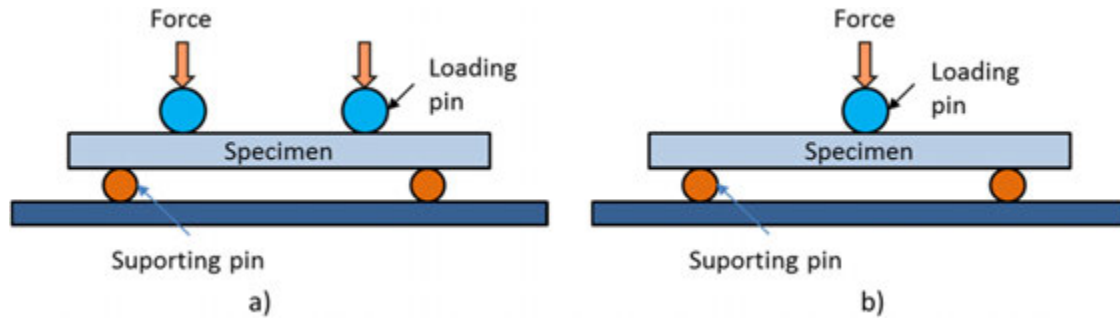


Fig. 11 Bending with the contact in three (a) or four points (b).

popular and is often performed due to the simplicity of sample preparation and the test method itself. Bend testing can serve for monitoring the quality of a certain material and comparing ceramic composite materials to each other (Hodgkinson, 2000).

The bend testing can be performed with three- or four-point contacts (Fig. 11) with different span lengths between the supports. If the test is performed with the contact in three points, the maximum sample stress will be in the middle of the sample, i.e. where the bending force acts. When bending with a four-point contact, the maximum stresses will be in the middle part of the sample, between the points where the bending forces act. The test sample will be under higher stress if the bending is performed at three points. It is impossible to compare the results obtained with these methods. From a stress standpoint, a four-point test is a better one of these two methods, but a three-point test is easier to do (Park and Seo, 2011). Bending strength is the stress on the surface of the sample during fracture, which should be accompanied by the fibers breaking, not by interlaminar shearing. Samples with a rectangular cross-section, a constant width and thickness, with free choice of dimensions (thickness 1–25 mm, width 10–25 mm and length 50–1800 mm) are most often used. The ratio of span length to thickness should be large enough to provide bending rather than shearing (ASTM C1341 recommends a ratio of span to thickness: 16:1, 32:1, 40:1, and 60:1). The bending speed should be such that bending to fracture lasts from 30 to 180 s (1–5 mm/min). The bend testing of CMCs is generally limited to samples with fibers placed parallel to the longer side of the sample. If the fibers are crossed with planar and spatial weaving, then this restriction does not apply (Freiman and Mecholsky, 2012). A universal testing machine can record discrete values of load and displacement in small load intervals, in the area of linear dependence, on the basis of which it is possible to determine the flexural modulus. In general, bend testing of CMCs is identical to the bend testing of other composite and structural materials (Carlsson, 2013).

Testing at elevated temperatures essentially does not differ from testing at room temperature, but it requires more attention when choosing the materials and designing the supports. The device must retain the appropriate mechanical properties and have adequate resistance to corrosion at high temperatures in the test atmosphere. In addition, the thermal expansion of the support material must be taken into account (Gyekenyesi, 1998).

Shear Testing

Shear strength is a basic property of composite materials. Shear strength is the stress a material can withstand before it begins to break down by delayering or fracture of the layers. The aim of shear testing is to determine the shear strength and shear modulus. The relationship between stress and strain during shearing till fracture is not linear over the entire range (Daniel and Ishai, 2006).

Over the past fifty years, several shear test methods have been developed, but only two have been standardized for fiber reinforced ceramic materials (ASTM C 1292): in-plane shear strength (IPSS) better known as the Iosipescu Shear Test Method (ASTM D 5379) and interlaminar shear strength (ILSS) also known as Double-Notched Specimen (DNS) Compression test of composites (ASTM D 3846). The main disadvantage of most existing test methods is the lack of a pure and uniform shear state (Hodgkinson, 2000). Only by testing a thin-walled pipe with a torsional load it is possible to achieve a purely uniform shearing, but this test is rarely performed due to the existence of numerous shortcomings. Making a pipe sample is quite complicated and requires special equipment and expertise. Such pipe is relatively brittle and usually does not represent material form used for real elements. The testing should be done on machines that can exert torsion, but such machines are much rarer than those with an axial load. In addition to the two listed tests, the following shear tests are also used:

- (1) Rail Shear Test Method, (ASTM D 4255).
- (2) V-Notched Rail Shear Test Method, (ASTM D 7078).
- (3) $[\pm 45]_s$ Tensile Shear Test Method (ASTM D 3518) and
- (4) Short-Beam Shear Test Method (ASTM D 2344).

The aforementioned tests are standardized primarily for composite materials with a polymer matrix but are also used for CMCs. In addition to these tests, there are others, such as: Torsion tube, Torsion of solid circular bar, Torsion of solid rectangular bars, ARCAN, Picture frame, Cross beam and cruciform specimen, Slotted or notched shear, Plate twist, Four point ring twist, Split ring

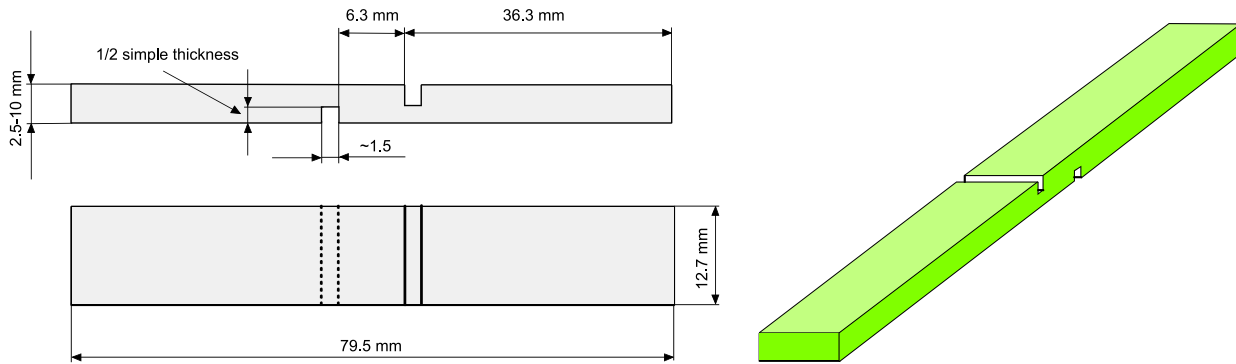


Fig. 12 Sample layout for the DNS test.

shear tests, Slotted tension-compression test, Block shear, Lap shear, Button torsion and Slant shear, but they did not find a wide application (Chaterjee *et al.*, 1993a,b).

Double-notched specimen (DNS) compression method (ASTM D 3846)

The Double-Notched Specimen Compression test is performed on samples that have two asymmetric notches made across the width of the sample on opposite sides (Fig. 12). The notches are ~1.5 mm wide and half the sample thickness deep. The front sides of the sample must be parallel to each other and perpendicular to the length of the sample. ASTM D 3846 stipulates that the sample length should be 79.5 mm, the width 12.7 mm, and the thickness should be in the range of 2.5–10 mm. The distance between the notches is 6.4 mm.

Such samples are placed in a special device (Fig. 13) which is mounted on a universal testing machine. The screws on the locking plates should not be tightened, because the sample has to slide freely (without friction) when compressed (Hodgkinson, 2000). The design of the device must ensure that the sample does not bend when compressed (Carlsson *et al.*, 2000). The sample is compressed from the front sides until the fracture occurs between the notches along the central part of the sample. Compressing should be performed at a speed of 1 mm/min.

The shear strength R_S is calculated by the following equation:

$$R_S = \frac{F_{max}}{bl},$$

where F_{max} represents the maximum force required to cause fracture, b is the width of the sample and l is the distance between the notches.

The strength related data obtained by this method has little scatter. Higher values of strength occur when the depth of the notch is less than or greater than half the sample thickness (due to the increase in cross section, which is why it is necessary for the notches to have the correct dimensions) (Jenkins, 1998).

Iosipescu shear test method (ASTM D 5379)

The Iosipescu shear test method is based on the original work of Romanian scientist Nicolae Iosipescu. He used this test for shear testing metal materials. It was not until the 1980s that this method began to be used for composite materials and in 1993 the method became the ASTM standard (ASTM D 5379) for composite materials. Analysis of the sample under load showed that there was a uniform state of almost pure shear stress between the notches (Hodgkinson, 2000).

This test uses a rod-shaped sample, with a rectangular cross-section. There are two V notches on the longer sides of the sample, with an angle of 90° and a depth of 4 mm. Standard samples are 76 mm long and 20 mm wide and up to 5 mm thick. Slightly lower values of shear strength and shear modulus are usually obtained when the thickness is greater than 5 mm. For the testing of samples thicker than 10 mm it is more beneficial to use an asymmetric four-point band (AFPB) test (Carlsson, 2013). The direction of fiber propagation in the sample can be the direction of the sample length or perpendicular to it (the direction of the sample width). The shear strength will significantly depend on the direction of fiber propagation (Walrath and Adams, 1983). The layout and dimensions of the standard sample are shown in Fig. 14.

The sample is placed symmetrically on a testing device, which is mounted on a universal testing machine. Sample centering is achieved with a centering pin. Vertical alignment of the sample is achieved with wedges that are moved by screws. The wedges are not clamps and should not be tightened to the sample. The test is performed by pressing on the right part of the device, while the left part remains stationary. This causes the sample to shear along the surface between the notches. The test is performed at a speed of 2 mm/min and it lasts until the sample is destroyed. It is possible to mount a camera on the testing machine and record the testing process for latter analysis. The device is simple and together with the sample is relatively small in size and the testing process itself is simple, altogether making this method very popular. The schematic diagram and layout of the Iosipescu device are shown in Fig. 15.

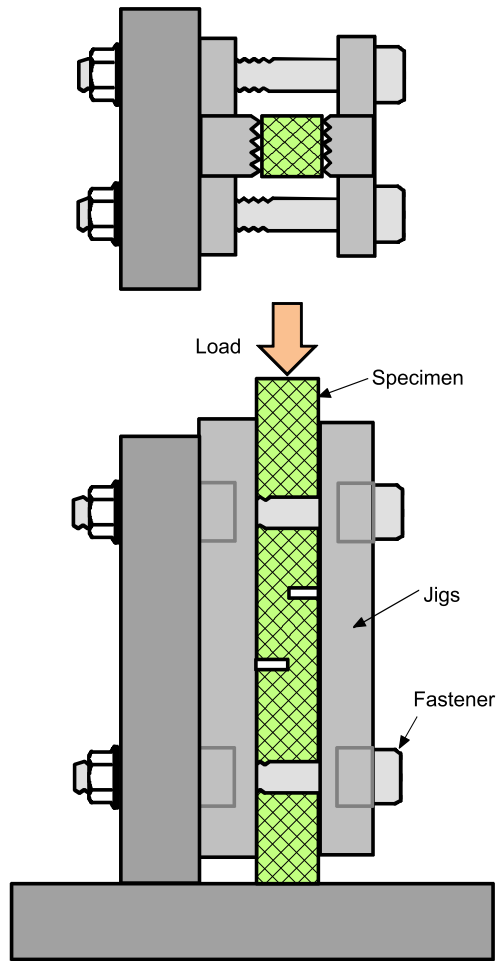


Fig. 13 Test fixture for the double-notched compression specimen.

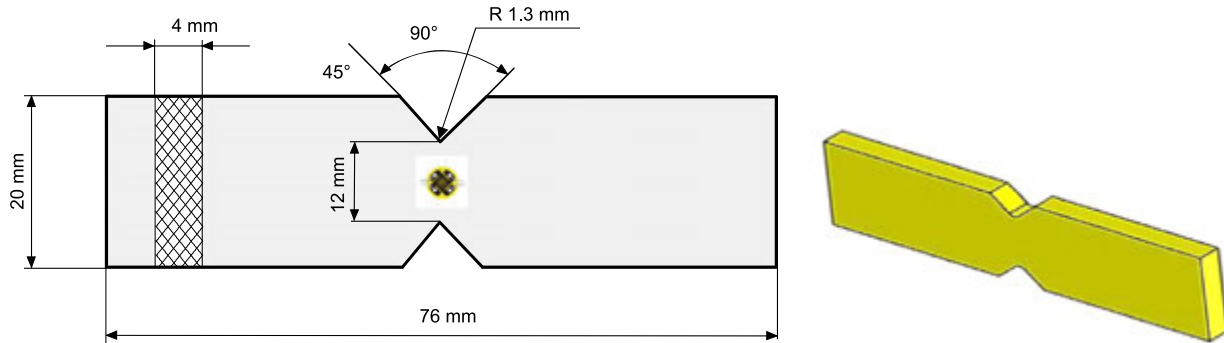


Fig. 14 Iosipescu shear test sample.

Shear strain is measured using strain gauges that are adhered between the notches, usually on both sides of the sample. Two strain gauges are adhered at an angle of 45° to the axis of the sample on each side. Based on the obtained shear strain and the load of the sample, a diagram of shear stress and strain can be drawn (Staab, 2015).

The shear strength R_s is calculated by the following equation:

$$R_s = \frac{F_{max}}{wh},$$

where F_{max} is the maximum force required to cause fracture, h is the sample thickness and w is the distance between the notch tips.

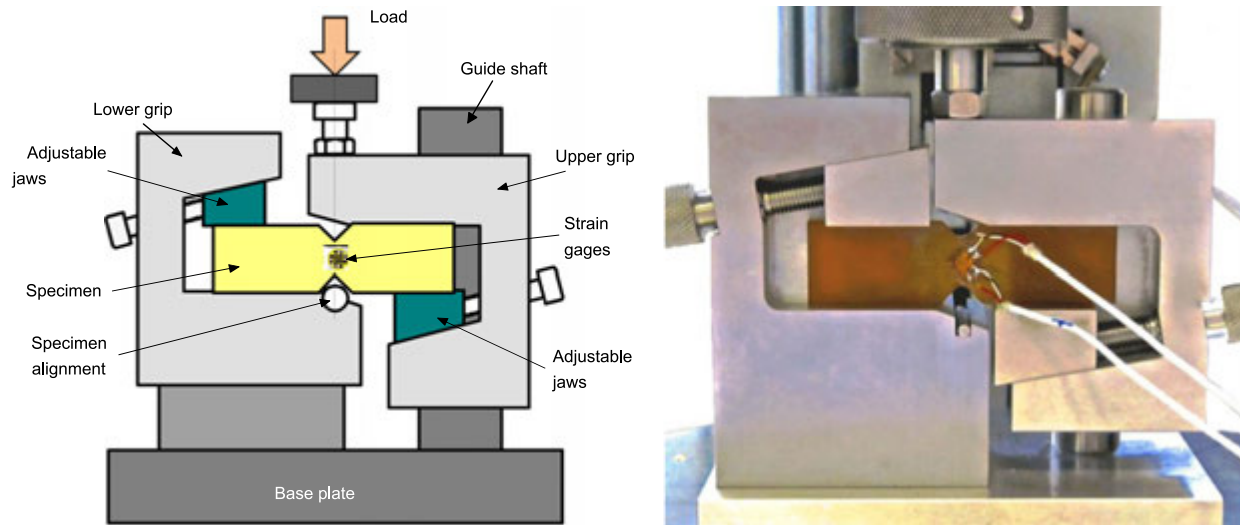


Fig. 15 Schematic diagram and layout of the Iosipescu device.

Shear strain γ represents the absolute value of the sum of measured strains:

$$\gamma = |\epsilon(+45^\circ)| + |\epsilon(-45^\circ)|.$$

The shear modulus G is determined by the following equation:

$$G = \frac{\Delta\tau}{\Delta\gamma} = \frac{\Delta F}{wh(\epsilon_{+45^\circ} - \epsilon_{-45^\circ})}, \text{MPa}$$

where ΔF is the change in load, $\Delta\epsilon_{+45^\circ}$, $\Delta\epsilon_{-45^\circ}$ is the change in deformation at an angle of $+45^\circ$ and -45° measured in the linear part of the stress-strain diagram (τ - γ).

Rail shear test method

This is a very popular method used to determine the planar shear properties of composite materials. Rails are placed on the edges of the sample with an appropriate fastening. There are two types: two-rail fastenings and three-rail fastenings (ASTM D4255). Both of these test methods require relatively large samples compared to other test methods (Hodgkinson, 2000).

Two-rail shear test method

This device was developed at the beginning of the second half of the twentieth century for testing plywood. As a consequence, it has some inconsistencies when used for testing composite materials. The layout of the device is shown in Fig. 16. The sample is placed at an angle (7° according to ASTM D4255) in relation to the load axis, which does not have any special technical explanation, which is why this device is sometimes made without inclination (Chaterjee et al., 1993a,b).

The test sample is quite large (as much as eight times larger than the Iosipescu sample), which is not economically viable, regardless of the fact that a larger volume of material is involved. The test sample is a rectangular plate measuring $74 \div 76 \text{ mm} \times 149 \div 151 \text{ mm}$ (Fig. 17). The thickness of the sample is free and is usually $1.3 \div 3.2 \text{ mm}$, depending on the material. There are six rail mounting holes on the sample, which is not very favorable due to the possible stress concentration and damage to the test material. There are more efficient ways to attach the sample today (e.g., using surfaces with sprayed tungsten carbide particles) (Carlsson, 2013).

Despite the disadvantages, this method has a number of advantages over other methods. There is almost a pure and uniform shear load acting on the test sample between the rails (on the part of the sample with a width of 12.7 mm). When testing uniaxial composites, the fibers can be oriented parallel (90° orientation) or perpendicular (0° orientation) to the rails. Orientation perpendicular to the rails is much more desirable because it reflects the effect of fibers pull out and fracture, while in the parallel orientation of the fibers there is mainly shearing through the matrix (Adams et al., 2003). There are no restrictions for the testing of cross-ply composites, either. It is important to achieve good sample tightening so that the rails do not slip and the screws do not rest on the holes, which would lead to local stress concentration and premature fracture of the sample. If it is necessary to measure the deformation, a strain gauge is adhered in the center of the sample. The sample may be subjected to tensile stress or compression, but compression is preferred. The test speed is 2 mm/min.

The shear strength R_S is determined based on the equation:

$$R_S = \frac{F_{\max}}{Lh}$$

where $F_{\max}$ is the maximum force required to destroy a sample of length L and thickness h .

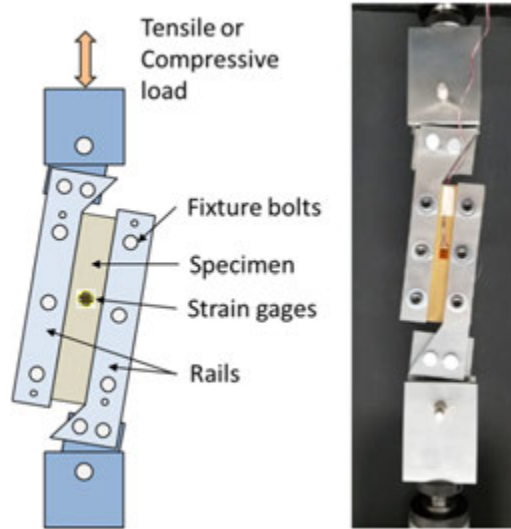


Fig. 16 Layout of the two-rail testing device.

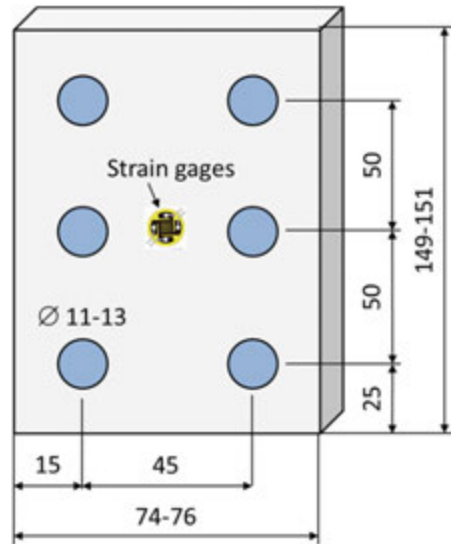


Fig. 17 Layout of the two-rail test sample.

The shear modulus G is determined by the following equation:

$$G = \frac{\Delta\tau}{\Delta\gamma} = \frac{\Delta F}{2Lh\Delta\epsilon_{45}}$$

Where ΔF is the change in force and $\Delta\epsilon_{45}$ is the change in deformation by $+45^\circ$ or -45° , depending on the placement of the strain gauge. If 2 strain gauges are placed (under $+45^\circ$ and -45°) then the deformation is calculated as the average of the two measured values.

Three-rail shear test method

Shear testing with a three-rail device is very similar to the previous testing, but is somewhat less used in practice, due to the larger dimensions and complexity of the device and the test sample. The dimensions of the sample are even larger and are about $150 \div 153 \text{ mm} \times 139 \div 141 \text{ mm}$. There are 9 holes in the sample, as shown in **Fig. 18**.

The middle row of holes serves to attach the middle pair of rails to the sample. Loading of the sample is achieved by the force acting on the middle pair of rails, while the outer pairs of rails are stationary and attached to the base plate which rests on the testing machine. The shear force is transmitted from the machine to the sample through friction between the rails and the sample. The sample may be subjected to compressive or tensile stress, but compression is predominant (Carlsson, 2013). The layout of the

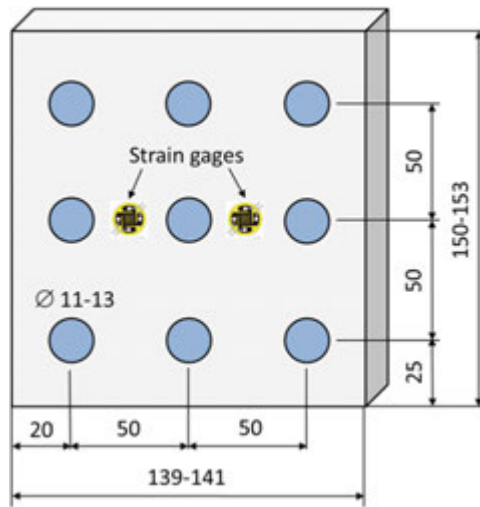


Fig. 18 Layout of the three-rail test sample.

three-rail device is shown in **Fig. 19**. Strain gauges are placed on the sample at an angle of 45° to the sample axis, as shown in **Fig. 19**.

The shear strength R_S is determined based on the equation:

$$R_S = \frac{F_{max}}{Lh},$$

The shear modulus G is determined by the following equation:

$$G = \frac{\Delta\tau}{\Delta\gamma} = \frac{\Delta F}{4Lh\Delta\epsilon_{45}}$$

where all the variables in these two equations are as previously given.

V-notched rail shear test method

The V-Notched Rail Shear Test Method was developed by combining other shear tests into one, while retaining the good and eliminating the poor characteristics of other tests. Using a sample without holes (compared to the Rail Shear Test Method) eliminates the risk of premature fracture due to the stress concentration and simplifies sample preparation (Carlsson, 2013). The sample, according to this test, is almost three times larger than the Iosipescu sample, and provides a much larger volume of the tested material, and thus greater accuracy. This sample is not loaded at the edges, unlike the Iosipescu sample, so there is no danger of crushing, and due to the size of the notch, there is a high probability of fracture at the narrowed part where it is almost pure shear stress (Karny, 2019). The advantage of this test is that it can be used to obtain very high shear strength (> 500 MPa), much more than other tests (Matthew, 2018).

This testing method is described by ASTM D7078. The sample dimensions are shown in **Fig. 20**. The length of the sample is 76 mm and the width is 56 mm, while the thickness of the sample is free and depends on the thickness of the tested material (it is recommended, when possible, for the thickness of the sample to be between 2 and 5 mm). Right-angled notches, both 12.7 mm deep, are made on both longer sides of the sample, symmetrically. In order to measure the sample deformation, strain gauges (usually 2) are placed at an angle of $\pm 45^\circ$ in relation to the sample axis and centered between the notches. The samples are cut from the tested material so that the fiber direction coincides with a longer sample axis (0°) or is normal to it (90°).

The test is performed using a two-part device that the sample is attached to (**Fig. 21**). Fastening is performed with two compression plates on each side, which are tightened with three screws. The surfaces of the compression plates and the clamping forces should prevent the sample from slipping. The samples should be placed symmetrically so that the tips of the notches coincide with the load action axis. This is achieved by temporarily placing appropriate spacers when placing the sample. The test is performed by tightening the left and right part of the device until the sample is destroyed.

The test speed should be such that the sample breaks within 1–10 min (~ 2 mm/min). The test is performed on 5 or more samples (depending on the desired accuracy of the results) if a sufficient amount of material is available. Testing on an increased number of samples increases the cost of testing, so it should only be done when necessary.

The shear strength R_S and shear strain γ , as well as the shear modulus, are calculated in the same way as for the Iosipescu Shear Test Method.

The shear strength R_S is calculated according to the equation:

$$R_S = \frac{F_{max}}{wh},$$

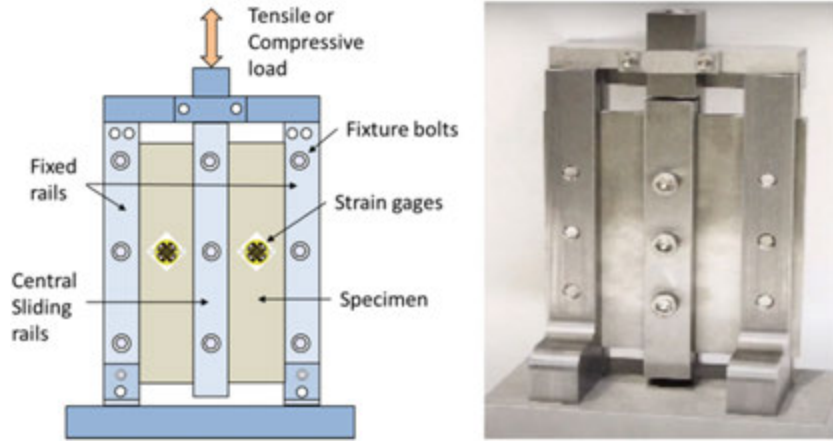


Fig. 19 Layout of the three-rail testing device.

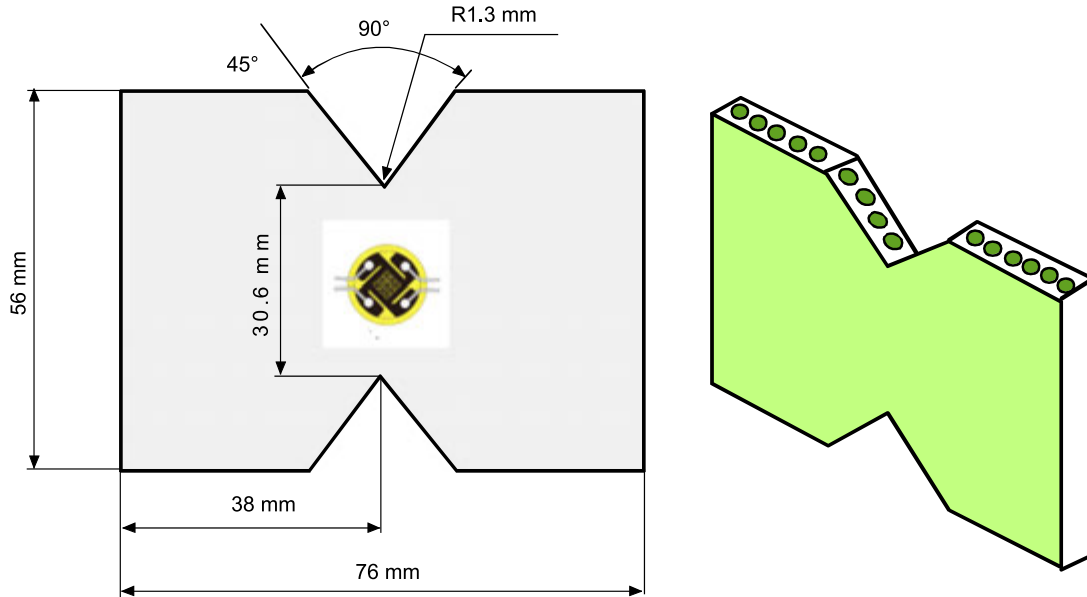


Fig. 20 Layout of the V-notched rail shear test sample.

Shear strain γ represents the absolute value of the sum of measured strains:

$$\gamma = |\varepsilon(+45^\circ)| + |\varepsilon(-45^\circ)|,$$

The shear modulus G is determined by the following equation:

$$G = \frac{\Delta\tau}{\Delta\gamma} = \frac{\Delta F}{wh(\varepsilon_{+45^\circ} - \varepsilon_{-45^\circ})}, \text{MPa}$$

where F_{max} is the maximum force required to destroy the sample, w is the distance between the notches, x is the thickness of the sample, ΔF is the load change, $\Delta\varepsilon_{45^\circ}$, $\Delta\varepsilon_{-45^\circ}$ is the change in deformation at an angle of $+45^\circ$ and -45° measured in the linear part of the stress-strain diagram (τ - γ).

Short-beam shear test method

This method for testing the shear strength of composite materials is frequently used, due to its simplicity. It is a three-point bending test with a small span between the supports. The small span between the supports causes a large-scale shearing in the middle plane of the sample which leads to interlaminar shear destruction. Therefore, this test is considered an interlaminar shear strength test. The strength determined by this test can be used for the quality control of composite materials or their processing. It can also be used for comparative testing of materials, but the obtained strength cannot be used for the numerical calculations in analysis of components (Carlsson, 2013).

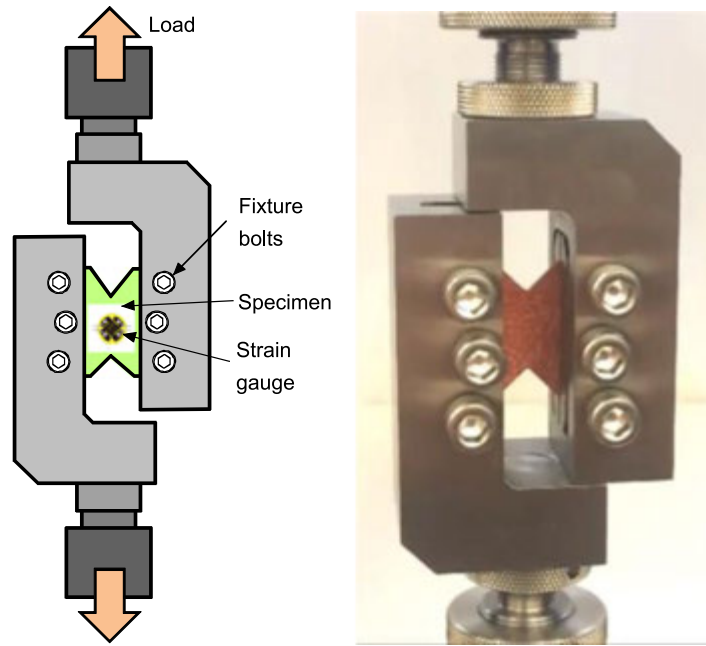


Fig. 21 Layout of the V-Notched Rail Shear Test device.

The test is performed according to the ASTM D2344 standard and consists of placing the sample on two supports and bending it with the help of a loading nose placed symmetrically between the supports. The bending device is mounted on a universal testing machine. The samples may be straight or curved with a central angle under 30° (Fig. 22). If the samples are straight, the supports are in the form of a cylinder with a diameter of 3 mm, and the loading nose is a cylinder with a diameter of 6 mm (Fig. 22a), and if the samples are curved, then the supports are in the form of a sliding plate and the loading nose is also in the form of a cylinder with a diameter of 6 mm (Fig. 22b). The test sample is quite small, so it requires little material. The aforementioned standard recommends sample dimensions of $39 \div 41 \times 11.9 \div 12.1$ mm and thickness $5.7 \div 6.3$ mm. In addition, the following geometric relationships are also recommended: sample length = thickness $\times 6$ and sample width = thickness $\times 2$. It is also recommended that the sample thickness should not be less than 2 mm.

The test is performed on at least 5 samples at the speed of 1 mm/min.

Simple uniaxial composite testing is most often performed. Based on this test, the interlaminar shear strength R_S can be calculated.

$$R_S = \frac{F_{max}}{\left(\frac{4bh}{3}\right)}, \text{MPa}$$

where F_{max} is the maximum load in N required to break the sample, b is the sample width in mm and h is the sample thickness in mm.

This method does not measure deformation or displacement and it is not possible to determine the shear modulus.

[$\pm 45^\circ$]ns tensile shear test method and 10° off-axis test method

The uniaxial tensile test [$\pm 45^\circ$]ns is a simple but fairly accurate method for determining the shear strength and shear modulus of uniaxial composite materials. Shear stress is determined based only on the applied tensile load, and shear strain is measured in two directions (longitudinal and transverse) using strain gauges. During the tensile testing a biaxial stress state is present in the sample, which influences the strength value reduction. This method is limited to fiber reinforced composite materials with a high elastic modulus and with fibers layout at $\pm 45^\circ$. Due to the insufficient accuracy of this method, for some classes of composite materials, it is often necessary to verify the obtained results with a more valid method of shear testing. Interlaminar stresses do not have their maximum values at 45° but at significantly smaller angles (Hodgkinson, 2000).

This method is performed by stretching the sample in the form of a strip (ASTM D3518) with the orientation of the fibers in relation to the direction of tensile load at an angle of 45° . The dimensions of the sample are the same as for tensile tests (length $175 \div 250$ mm, width $15 \div 25$ mm, while the thickness is free and depends on the thickness of the tested material (Fig. 23)). Tabs made of metal (Al, brass) or some other less brittle composite material can be glued at the ends of the sample in order to prevent possible crushing during clamping in the jaws of the testing machine.

The 10° off-axis test method is a method used to determine the shear properties of composite materials that is not described by any standard (Hodgkinson, 2000). This method is almost exactly the same as the [$\pm 45^\circ$]ns Tensile Shear Test Method, with the difference being that the fibers are oriented at an angle of 10° to the load axis (Fig. 24).

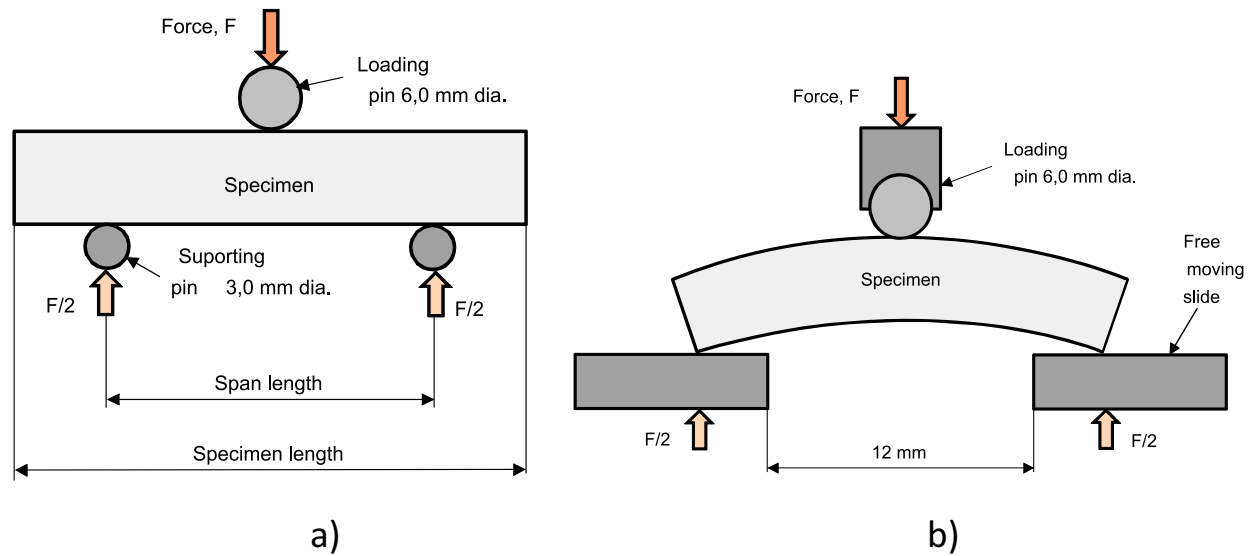


Fig. 22 Load diagram of (a) straight samples, (b) curved samples.

The angle of 10° was chosen to minimize the effects of the longitudinal and transverse stress components on the shear stress value. At an angle of 10° the shear deformation is close to its maximum value. It is proposed that the dimensions of the test sample should be similar to the dimensions of the sample for $[\pm 45]_s$ Tensile Shear Test Method (sample length 250 mm, width 25 mm and thickness 2 mm) (Hodgkinson, 2000).

Fiber/matrix interface properties testing

The fiber/matrix interface is very important for determining the final properties of the composite material, due to the following:

- (1) the interface occupies a very large space in a composite, and
- (2) the reinforcement and the matrix will form a system that is not in a thermodynamic equilibrium.

The general properties of the fiber/matrix interface and some of the tests for determining its mechanical properties will be described here. The interface between the reinforcement and the matrix can be defined as the surface on which parameters or properties are interrupted, such as atomic lattice, density, elastic modulus, thermal expansion coefficient, material strength, fracture toughness, etc. This means that the discontinuity appears abruptly, while it would be much more beneficial if the interface zone had a certain thickness through which a gradual interruption of properties would occur.

Two main types of bond at the interface are mechanical bond and chemical bond (Kim and Mai, 1998).

The mechanical bond creates adhesion of the matrix to the reinforcing fibers. Fig. 25 shows the ideal (a) and real (b) contact between the matrix and the fiber. If the matrix shrinks when cooling, this would cause the matrix to adhere to the fiber. Such a mechanical bond would make it difficult to pull the fibers out of the matrix (Chawla, 2013).

The chemical bond generally is characterized by diffusion. Solid solutions and compounds can form at the interface, which leads to a reaction between the fibers and the matrix within a zone of a certain thickness (Kim and Mai, 1998).

In general, mechanical bond is a low-energy bond compared to a chemical bond, i.e., the mechanical bond is less strong.

The strength of the bond between the fiber and the matrix influences the fracture behavior of the composite. If the bond at the interface is strong there will be no prevention of crack propagation which will lead to a brittle fracture of the composite. If the connection is too weak it can lead to debonding of the fibers from the matrix and eventually to larger pull out of the fibers, which is also not good. A fiber/matrix interface bond that is sufficiently strong and not too weak will only partially break and lead to a diversion of crack propagation through the matrix, as well as to bridging over the fibers. Such a bond will ensure absorption of supplied energy and increase the fracture toughness, which will prevent the catastrophic brittle fracture of the CMCs.

Proper control of interface properties is the key to obtaining a tough ceramic composite. Composite constituents must be chemically stable at both processing and exploitation temperatures. Any chemical interaction between the matrix and the reinforcement during processing will influence the strength of the interface bond, thus the possibility of debonding at the fiber/matrix interface and lead to fibers pull out. Therefore, it is necessary to ensure optimal interface strength and fracture toughness, i.e., the speed of energy release. The interface should be strong enough to transfer the axial load in the transverse direction, and yet weak enough for the transverse crack to extend along the interface leading to fiber debonding, pull out and fracture, thus providing toughness.

The interface property can be controlled in two ways:

1. Proper selection of fibers and matrix so that they form a thermodynamic interface during processing and during exploitation;

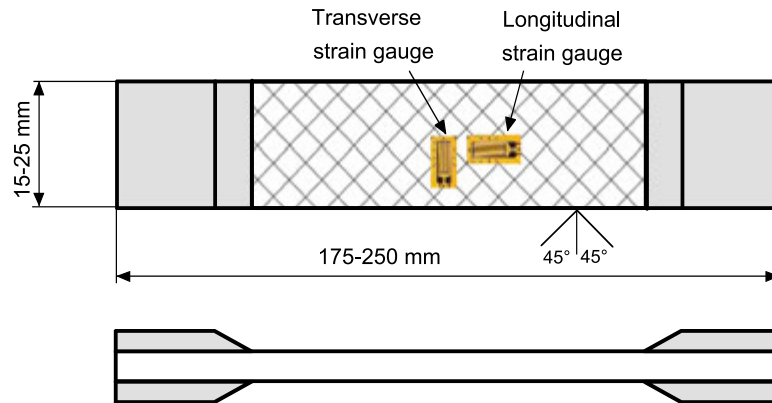


Fig. 23 Test sample for the $[\pm 45]_{ns}$ tensile shear test method.

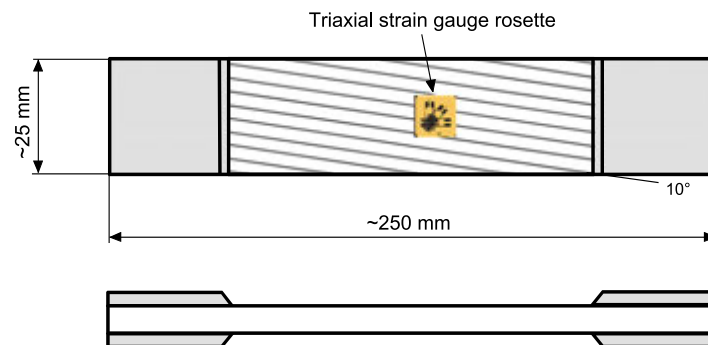


Fig. 24 Layout of the 10° off-axis test sample.

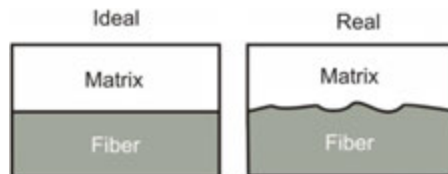


Fig. 25 Ideal and real interface bond.

2. Incorporating a coating between the fibers and the matrix that enables optimal strength by preventing unwanted chemical reactions at fiber/matrix interface (the choice of coating depends on the fiber, matrix, processing and exploitation requirements; coatings with carbon, silicon carbide, boron nitride and tin dioxide have been tested (Kim and Mai, 1998)).

The interface coating provides an easy and efficient way to customize the interface area. The fiber coating can also protect the fiber from mechanical damage during processing and exploitation. Ideally, it is possible to have a coating that does not interact with either the fibers or the matrix, and remains stable in both processing and exploitation. It is clear that the coating thickness will be an important parameter; with usual range of $0.1\text{--}1\text{ }\mu\text{m}$. Carbon and boron nitride are the most commonly used coatings. Silicon carbide, zirconium and tin dioxide are some of the possible coating materials (Belitskus, 1993).

It is almost impossible to eliminate the discrepancy in thermal expansion between the matrix and reinforcing phases (fibers and matrix). What can be done is to use this intrinsic property of a composite material to achieve a favorable thermal stress distribution in the composite by selecting phases, so that the residual stress existing after processing is the one that gives the desired final property of the composite. In particular, in composites with ceramic matrices, it is desirable to allow the cracks to divert to the fiber/matrix interface, thus facilitating the delayering of the interface. Such debonding and crack deflection at the interface are prerequisites for the pull out of fibers, all of which contribute to an increase in toughness of the composite. The type of interfacial bond (chemical or mechanical) as well as the nature and amount of the residual thermal stresses after composite processing will be very important. Since the choice of matrix and fibers is determined by the application of the composite, coatings are often applied to the fiber,

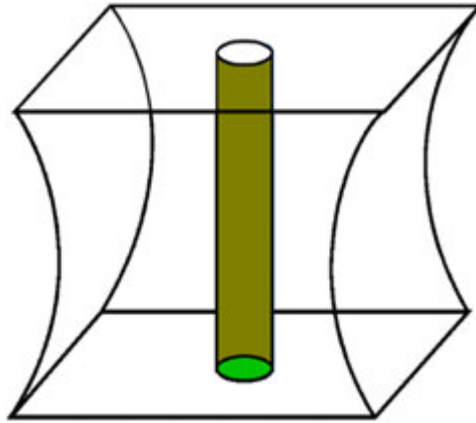


Fig. 26 Layout of a curved-neck test sample containing one fiber along its central axis.

suitable for a given composite system, in order to optimize the stress distribution and the fiber/matrix interfacial bond. In composites with a ceramic matrix, the appropriate interfacial coatings are selected to achieve primarily mechanical bonds (Kim and Mai, 1998). In a mechanically bonded interface, the degree of interface roughness becomes an important parameter.

Based on the aforementioned, it is obvious that knowing the quantitative measure of the strength of the fiber/matrix interfacial bond is very important, which led to the development of several tests for determining it. The most commonly used are:

- (1) Curved-neck sample test,
- (2) Bending test,
- (3) Pull-out and push-out fiber test.

Curved-neck sample test

For this test, a special mold is used to prepare a curved-neck sample containing one fiber along its central axis (Fig. 26). The sample is compressed and the debonding of fiber from the matrix is visually observed. The curved shape of the sample amplifies the transverse tensile stress at the fiber/matrix interface. The transverse tensile stress that leads to the debonding of the interface is the result of the matrix and the fibers having different Poisson coefficients. If the Poisson coefficient of the matrix is greater than the Poisson coefficient of the fiber then, when the curved-neck sample is compressed, a transverse tensile stress will occur in the center of the neck. The stress corresponding to the interface debonding can be measured and the interfacial bond strength can be calculated (Park and Seo, 2011). It is very important to ensure the parallelism of the fiber in relation to the central axis of the sample when preparing this type of sample. It is also necessary to provide a visual inspection to determine the point of debonding of the interface. This would limit the test use to transparent matrix materials, although acoustic emission technique overcomes this issue (Chawla, 2013).

Bending test

The bending test can be performed by two tests:

- (1) Transverse bending test and
- (2) Longitudinal bending test.

Characteristic of these tests is that they are very easy to perform but do not give accurate values of the interfacial strength (Chawla, 2013).

Transverse bending test

The test is performed by three-point bending with the fibers placed perpendicular to the length of the test sample (Fig. 27). The transverse strength at the contact between the fiber and the matrix corresponds to the fracture of the surface that is at the greatest distance and under the tensile stress.

Longitudinal bending test

For this test, the fibers are parallel to the length of the sample being bent at three points (Fig. 28). The maximum shear stress, in this case, occurs in the middle plane, and the maximum tensile stress occurs at the farthest (lower) surface. If the test were performed with a very small span between the supports, then the crack, caused by the maximum tensile stress at the rear, would continue to spread through the middle due to the maximum shear stress.

Interpreting this test is not easy. The test would not be valid if the fibers break due to tensile stress rather than shear stress, or in case of simultaneous occurrence of fracture due to tensile stress and shear stress, which is determined by inspecting the fracture surface after testing to see if the crack occurred along the interface and not through the matrix.

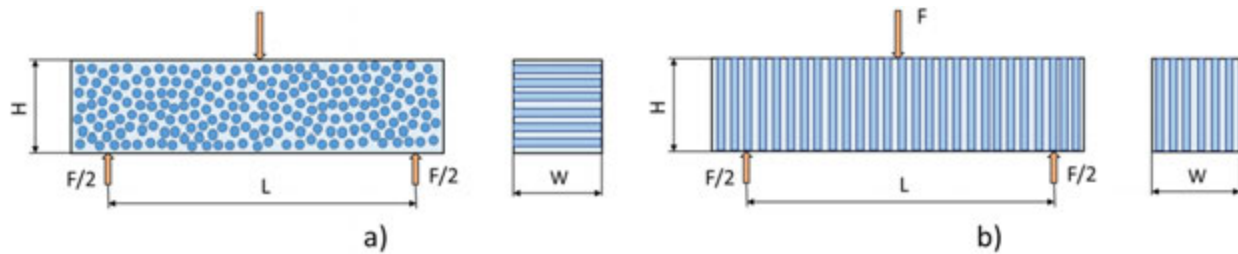


Fig. 27 Three-point transverse bending test: (a) fibers placed perpendicular to the loading direction; (b) fibers placed parallel to the loading direction.

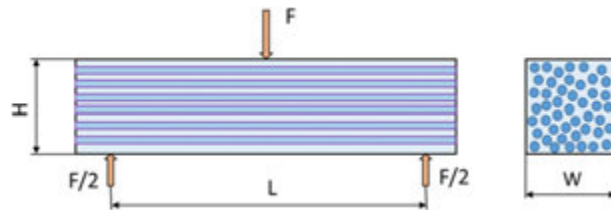


Fig. 28 Longitudinal bending test scheme.

Pull-out and push-out fiber test

Pull-out and push-out fiber tests serve to determine the maximum load required to break the mechanical and chemical interfacial bonds.

Single fiber pull-out test

Single fiber pull-out tests that are often used for PMCs, and less often for MMCs and CMCs, can provide useful information about interfacial strength. They are not very helpful in the case of commercially available composites because these cannot be used for testing. During the test, fibers must not bend, which significantly complicates the test (Chawla, 2013).

Fig. 29a shows the layout of the experimental sample for this test with a fiber of a certain length embedded in the matrix being pulled out by the appropriate pulling force. Making a single fiber test sample is often the most difficult part, which involves incorporating a part of a single fiber into the matrix. A modified variation of this procedure is to incorporate both ends of a single fiber into the matrix material (Fig. 29b), leaving the central region of the fiber uncovered. In both cases, the fiber is pulled out from the matrix in the tensile testing machine and the load in relation to the displacement is recorded.

The maximum load occurs when the interface between the fiber and the matrix is broken. Next, there is sliding friction while the fiber is being pulled out of the matrix, whereat the load is constantly decreasing because the length of the fiber in the matrix is also reducing. Therefore, this test simulates the fiber/matrix interface breaking which can occur in real composites and, more importantly, it gives the value of bond strength and the value of friction stress (Jarzabek and Dera, 2016).

Different Poisson coefficients between the matrix and the fiber lead to a radial stress on the interface which, due to its nature, is not constant along the fiber which complicates the analysis of this test.

Fiber push-out test

For this test, a sample is previously cut from the composite material perpendicular to the direction of fiber propagation. The sample can contain multiple fibers and its length should be significantly greater than the diameter of the fiber. The fibers are pushed through the matrix by an indenter that can be in a variety of shapes, as shown in Fig. 30 (Chawla, 2013). To perform the simplest form of this test, the devices for measuring microhardness according to the Vickers or Berkovich method can be used. It is also possible to utilize a nanoindenter or a universal tensometer in the compression mode. When pushing the fiber, the force will increase from zero to a maximum value required to break the fiber/matrix interface. This is followed by a period of sliding between the fiber and the matrix, until eventually the force starts to increase again when the indenter touches the matrix and begins to deform it. Thus, it is possible to separately determine the force required to break the interface and the friction force of the fiber sliding through the matrix (Park and Seo, 2011). If the test is performed using a nanoindenter, there is a possibility to measure extremely small forces and displacements. Consequently, very small amounts of material can be studied and, when determining the interfacial strength, certain assumptions need to be taken into account (Jarzabek and Dera, 2016):

- (1) Any elastic deformation of the matrix around the fiber is negligible,
- (2) There are no surface stress concentrations,

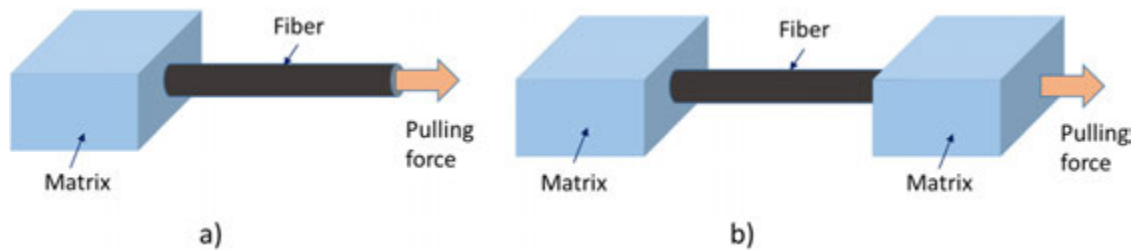


Fig. 29 Layout of the single fiber pull-out test; (a) fiber embedded in the matrix on one side, (b) fiber embedded in the matrix on both sides.

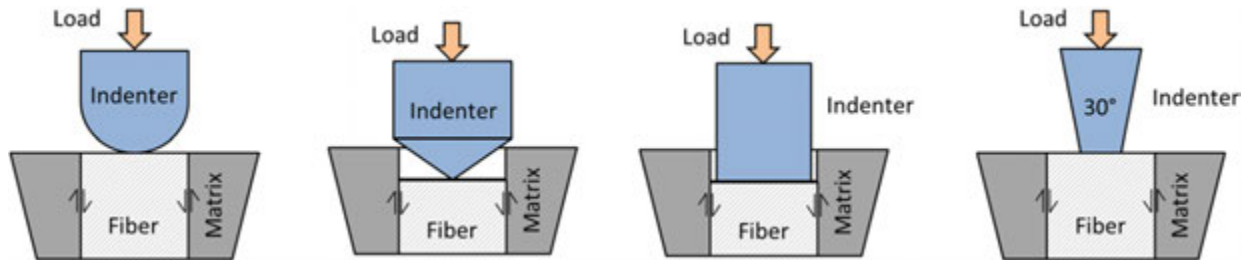


Fig. 30 Different forms of indenters for pushing out the fibers.

- (3) There are no changes in the diameter of the fiber resulting from the pressure of the matrix on the fiber due to difference in Poisson coefficients,
- (4) There are no residual stresses.

An advantage of this test is that the samples can be cut from commercially available composites, with the limitation being that it is not possible to test samples from 3D woven composites.

In addition to the aforementioned methods, there are other methods for determining and estimating the fiber/matrix interfacial strength. Some of them are: (Chawla, 2013).

- (1) Tensile test to assess the strength using the spacing between cracks on the matrix,
- (2) Laser spraying technique,
- (3) Compression test of small thickness sample between a hard and a soft plate, etc.

Improvements in individual methods are also possible through parallel analysis by using numerical simulations methods.

There is also the possibility of estimating the fiber/matrix bond and microstructural characterization of the interface area. Various sophisticated techniques such as electronic microscopy (HREM, TEM, AFM, SEM, CT, etc.) are available for that purpose. The interface area is extremely complex and variable, so the chemical composition of the components, the crystallographic and chemical nature of the interface area, the effect of processing conditions, etc. can greatly influence the properties and performance of composites (Chawla, 2013).

Standards

The tests used to examine composite materials are standardized by many organizations. The main international standards for testing composites are ASTM (American Society for Testing and Materials), ISO (International Organization for Standardization), and EN (European Standards). In addition to international standards, there are a number of manufacturer standards such as BSS (Boeing Specification Support), AITM (Airbus Testing Method) and others. In many cases, the methods described by different standards are basically the same, but there are some differences in the dimensions and clamping methods. Table 1 provides an overview of ASTM standards for testing composite materials with a ceramic matrix as well as for some tests of composite materials with a polymer matrix, based on which the testing of CMCs is performed.

Conclusions

Ceramic matrix composites (CMCs) are usually applied for elements that are subjected to compressive stresses, since their tensile properties are far beyond compressive ones. Accordingly, compressive tests are the mostly standardized ones, even though tensile tests are well developed. However, shear strength is also of the utmost importance for fiber reinforced composites. Range of static mechanical tests have been developed and standardized for general and specific purposes, in order to verify functional composite

Table 1 An overview of selected ASTM standards in relation to ceramic matrix composites

Standard label	Name of the standard
ASTM D3379	Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single-Filament Materials
ASTM C 1275	Test Method for Monotonic Tensile Behavior of Continuous Fiber-Reinforced Advanced Ceramics with Solid Rectangular Cross-Section at Ambient Temperatures
ASTM C 1358	Test Method for Monotonic Compressive Strength Testing of Continuous Fiber-Reinforced Advanced Ceramics with Solid Rectangular Cross-Section Specimens at Ambient Temperatures
ASTM C 1341	Test Method for Flexural Properties of Continuous Fiber-Reinforced Advanced Ceramic Composites
ASTM C 1292	Test Method for Shear Strength of Continuous Fiber-Reinforced Advanced Ceramics at Ambient Temperatures
ASTM D 5379	Standard Test Method for Shear Properties of Composite Materials by the V-Notched Beam Method
ASTM D 3846	Standard Test Method for In-Plane Shear Strength of Reinforced Plastics
ASTM D 4255	Standard Test Method for In-Plane Shear Properties of Polymer Matrix Composite Materials by the Rail Shear Method
ASTM D 7078	Standard Test Method for Shear Properties of Composite Materials by V-Notched Rail Shear Method
ASTM D 3518	Standard Test Method for In-Plane Shear Response of Polymer Matrix Composite Materials by Tensile Test of a $\pm 45^\circ$ Laminate
ASTM D 2344	Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates

properties, but also to establish the foundation for numerical simulations in design and prediction of composite functioning. Significant difference in mechanical testing of composites is related to different phases within a composite structure, thus imposing the need for different approaches. Mechanical properties of the composite are not sufficient for the comprehensive determination of their functional lives, as in the case of monolithic materials. Properties of the reinforcement phases are also significant, as well as the properties of the interphases between different phases. Fiber reinforcement is the most important for commercially used CMCs and fiber testing have been developed and even standardized in some extent, as well as the mechanical testing of the fiber/matrix interphase. Significance of the mechanical properties indicates a need to further investigate and develop more suitable mechanical tests for CMCs, especially in relation to cost efficient full simulation of real functional conditions in lab environments.

Acknowledgments

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Hardness and Non-Destructive Testing (NDT) of Ceramic Matrix Composites (CMCs)

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Introduction

In general, all non-destructive testing methods in material and product quality control are often referred to as defectoscopy. Defectoscopy (non-destructive) is a set of methods for finding internal defects within the material structure (caused by the production of the base material, the production of parts and assemblies, the operating conditions, etc.) in such a way that the tested material, components and devices remain undamaged after inspection, and if no inadmissible errors are detected in them, can be brought back to normal function.

The main goal of non-destructive testing is to determine the existence of irregularities in the material or to measure certain physical quantities of the material in order to characterize it (Czichos *et al.*, 2006). In professional literature, non-destructive defectoscopy often is not separated from the wider scope of non-destructive testing methods, where it dominates. In addition to defect detection, non-destructive testing of materials includes determination of surface roughness, hardness measurement, X-ray, electron and neutron crystallography, spectral analysis, X-ray spectroscopy, measurement of coating thickness, and other newly developed techniques (Zivic *et al.*, 2012a). Defectoscopy methods are commonly used in almost all types of production and usually represent one of the stages in the production technology. Laboratories for this type of control, in addition to laboratories for mechanical testing of materials, often represent the central places for product quality control (Oruč and Sunulahpaši, 2012). The test costs are reduced because the tested parts are not destroyed, so in case of a positive test result, these parts can be built into the final construction and exploited.

In fast-growing industry, where reliability requirements are increasing and where new and modern materials are being introduced, a growing range of non-destructive testing methods are playing an increasingly big role. These methods are used to evaluate defects in different materials, as well as to characterize material properties. The use of non-destructive methods leads to a better understanding of material behavior, which leads to an increase in the confidence of designers and their trust in the materials used. This means that the designer can choose a lower value of the safety factor without sacrificing reliability. Lower values of safety factors lead to a reduction in dimensions, which results in savings in the amount of used material. Non-destructive testing methods are also used for routine and periodic inspections of various industrial processes, especially in areas where new materials are applied whose properties and behavior are not widely known, as is the case with composite materials. This is especially significant in aerospace, military, nuclear, electrical and chemical industries (Prakash, 2012).

Composite materials are advancing more and more and are being used in the production of increasingly efficient and economical products with superior specific properties. This is especially true for long-fiber ceramic composite materials, which are superior to other materials in terms of high operating temperatures and low density. The production of composite materials includes many processes, where different types of defects can occur, which causes significant safety problems. Detection and assessment of internal defects are especially important for maintaining the structural integrity of composite materials that are, by nature, inhomogeneous and anisotropic. Errors and defects can occur at different locations and at different scales, which make it difficult to track them all and can lead to complex damage mechanisms. The initiation of defects inside the composite can lead to a decrease in the strength, stiffness and lifespan of that component. That is the reason why non-destructive testing is important and used in order to reduce the possibility of errors and avoid disturbances and delays in the production process. Damage to already finished products, invisible to the visual or surface inspections, can occur in operation due to variable mechanical and thermal loads. In this case, non-destructive testing is very important, yet again. There are a number of non-destructive testing methods proven to be very effective in ensuring the quality of composite products throughout their life cycle (Wang *et al.*, 2020; Ibrahim, 2014; Yao *et al.*, 2014).

This article will provide an overview of non-destructive testing methods for the detection and assessment of defects and errors, as well as methods for measuring hardness, though without a detailed and complete description of all methods, which is beyond the scope of this text. There are several good reviews in literature related to non-destructive testing methods for composite materials (Czichos *et al.*, 2006; Babcsan *et al.*, 2014; Angker and Swain, 2006; Balageas and Roche, 2014). Also, American Society for Testing and Materials (ASTM) has developed more than 130 standards, guides, and procedures, which contain technical specifications, criteria, requirements, procedures, and good practices for many non-destructive testing methods (Fahr, 2014).

Hardness Measurement

Hardness is defined as the resistance of a material to the surface penetration by the other, harder material (indenter). Hardness testing is a simple and fast technique, which has long been used to test all materials and control their quality. The hardness test is probably the most commonly used mechanical property test for metals, polymers and ceramics. Hardness is correlated with some mechanical properties, despite the fact that mechanical properties determined by the hardness test are not unambiguously defined

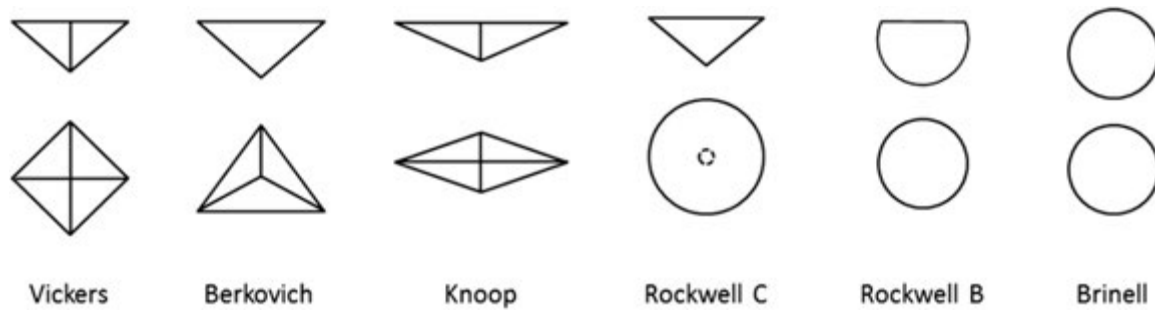


Fig. 1 Different shapes of hardness indenters.

physical quantities. The mechanical properties correlated with hardness are primarily strength, abrasion resistance, resistance to plastic deformation, modulus of elasticity, and fracture toughness (Chandler, 1999). The hardness of ceramics, and subsequently of ceramic composite materials, is determined by its chemical composition, also including porosity and grain size (Elssner, 1999).

The hardness test only slightly damages the surface of the test object, so it can generally be classified as non-destructive testing. The sample does not need any specific preparation for this test, but its surface needs to be properly prepared. There are three general types of hardness measurements, depending on how the test is performed:

- indentation hardness,
- resistance to scratching or scratch hardness,
- elastic rebound or dynamic hardness.

There are several methods of measuring indentation hardness, depending on the shape of the indenter, its material, the range of applied force and the time and mode of loading. There are macro-, micro- and nano-hardness according to the scale of the applied load. "Macro" test refers to a test where the load is > 10 N; similarly, the "micro" test refers to a load ≤ 10 N, and if the load is very small (less than 300 mN) then it is a "nano test" (Herrmann, 2011). The hardness testing can be static or dynamic. Static methods are most commonly used and these are hardness tests by: Brinell, Vickers, Knoop, Rockwell and Berkovich. Depending on the method selected, the hardness is labeled as HB, HV, HK, HR, respectively, where each method provides a different number. Each type of measurement is based on its own scale. However, conversion between different methods is possible for practical purposes but it is only approximate. The unit for hardness is GPa or N/m². Traditionally, Rockwell and Brinell tests fall into the macro category, while the Knoop test is used for micro-indenting tests. Vickers tests can be macro or micro tests depending on the load value. The basic concept used in all of these tests is applying a fixed indenting force to the appropriately shaped indenter in order to determine the material's resistance to penetration (Czichos *et al.*, 2006). If the material is hard, a relatively small or shallow indentation will form, and if the material is soft, a rather large or deep indentation will occur. The shape of the indenter and the consequent indentation, for different methods, is given in Fig. 1.

Generally, traditional indenting methods, such as Rockwell, Vickers, Knoop and Berkovich, can be used for materials such as ceramics that are harder than metals and their alloys. The size of the indentation or depth of penetration of the indenter into the material will be smaller in that case, but it needs to be large enough to be measured with appropriate accuracy, to determine the hardness value number. Since ceramics are brittle, deformation and processes under load are somewhat different than for metals (Zivic *et al.*, 2013). In most cases, cracking of the sample material occurs, especially at the corners of the indentation, but the hardness measurement still has to be performed in the presence of cracking, and the acceptability of the results is determined by whether the cracking obscures the true size of the indentation. This will vary from material to material, depending on its hardness and the magnitude of the force with which the indentation was made (Clinton and Morrell, 1987).

The hardness of ceramics and ceramic matrix composites (CMCs) is usually determined using the Vickers or Knoop method, and for research purposes the Vickers, Knoop and Berkovich method, while the Rockwell and Brinell methods are not suitable and are relatively rarely used (Elssner, 1999).

The Brinell Method

The Brinell method is performed by pressing a ball of diameter D , under the load F , into the surface of the material whose hardness is being measured. After unloading and removing the ball, an indent in the shape of a calotte of diameter d remains in the material (Fig. 2).

The measure of hardness according to the Brinell method is the ratio of the force, which acts on the appropriate ball-shaped indenter and the surface of the residual indentation calotte on the object's surface, as given in Eq. (1).

$$HB = \frac{F}{A} = 0,102 \frac{2F}{\pi D(D - \sqrt{D^2 - d^2})} \quad (1)$$

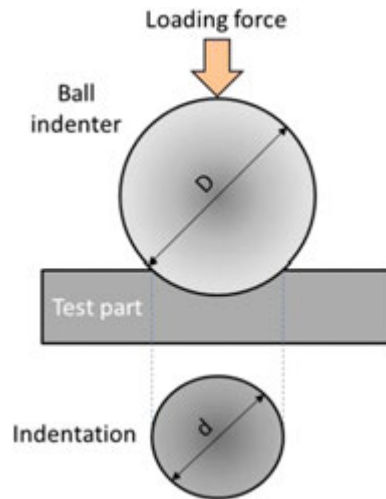


Fig. 2 The Brinell hardness measurement scheme.

For the Brinell hardness test, the indenter is a steel ball with a diameter of 10, 5 or 2.5 mm, and exceptionally, the diameter of the ball can be 1 or 2 mm. The material of the ball is hardened steel with a hardness of 850 HV or hard metal (Widia). The ball diameter and the indenting force are determined from the requirement $F/D_2 = \text{const}$. The F/D_2 ratio is selected depending on the type of material whose hardness is measured. The measurement is valid if the diameter of the indented calotte d is 0.25–0.5 of the diameter of the ball D (Herrmann, 2011). The duration of the indentation depends on the type of material whose hardness is measured, while the load increases gradually, given that it is the static test method. Traditional hardness measuring device achieves a static force action on the indenter, through a system of levers that altogether act on a sample placed in a sample holder. Usually, the same device is used for the Vickers hardness measurement, though the indenter and the required load have to be changed.

The Vickers Method

Vickers hardness is defined as the ratio of the force F acting on the diamond indenter (regular four-sided pyramid shape) and the surface A of the indentation (on the surface of the object whose hardness is being measured), as given in Eq. (2), and shown in Fig. 3.

$$HV = \frac{F}{A} \cong 1,854 \frac{F}{d^2} \quad (2)$$

where F is the load in (N), and d is the average measured value of the indentation's diagonal in (mm). The coefficient 1.854 refers to the geometry of the Vickers indenter.

The indenter is made of a diamond in the shape of a regular four-sided pyramid with an angle at the top of $136^\circ \pm 0.5^\circ$. The sides of the indenter have to be properly machined and inclined evenly towards the axis so that the connection line between the opposite sides is no longer than 0.002 mm. The magnitude of the indenting force depends on the type and thickness of the material and is selected based on the recommendations (Majstorović and Đukić, 1986). If the Vickers test is performed with low indenting forces (≤ 10 N) then that is microhardness. The required duration of indentation into the sample's surface has to ensure a uniform increase in force up to the selected value (Czichos *et al.*, 2006).

Ideally, the indentation has a square shape with identical diagonal lengths, but in reality, many materials have a deformed indentation with non-identical diagonals, which makes it difficult to measure and determine hardness. The established rules are: the indenting is never performed at the ends of the sample because of the “edge” effect, and the distance between two indentations has to be at least 3 times bigger than the indentation's diagonal (Herrmann, 2011). The test is repeated several times and the average of the measured diagonals is taken.

A load of 30 daN is usually used for metals and their alloys. For ceramics and CMC materials, this load is too high and it would cause local catastrophic failure or even destruction of small pieces whose hardness is being measured (Sidjanin *et al.*, 2007). Therefore, it is necessary to perform the test with significantly lower load values. Experience has shown that a load of 2.5 daN should be considered the maximum acceptable load for hardness testing of ceramic materials, in order to avoid rough fracture for the most of ceramic materials (Clinton and Morrell, 1987). Fig. 4(a) shows the damage at a load of 5 daN with the crack formation at the corners of the indentation, which leads to incorrect results. In contrast, lower loads give smaller indentations, which are more difficult to measure, but the risk of cracking is significantly lower (Fig. 4(b)).

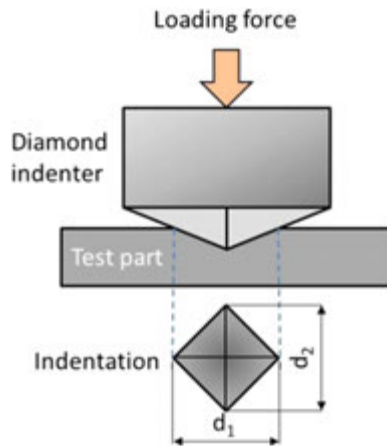


Fig. 3 Vickers hardness measurement scheme.

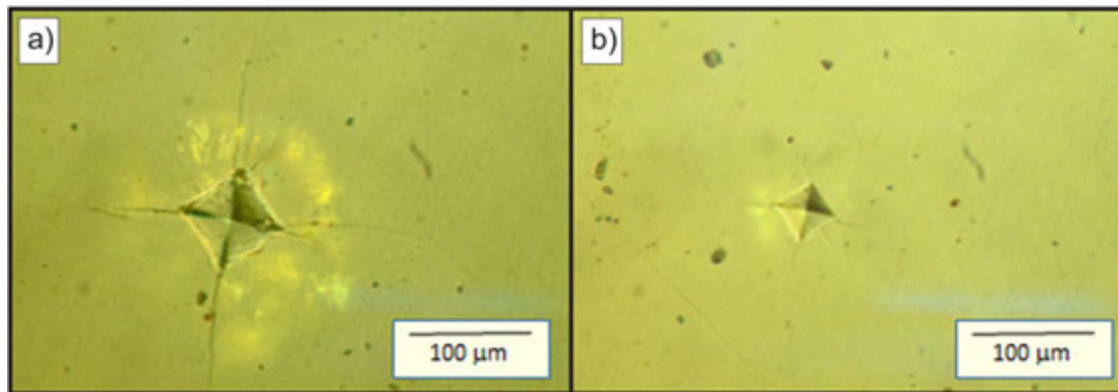


Fig. 4 Indents made by the diamond pyramid at loads of: (a) 5 daN and (b) 0.5 daN.

The Rockwell Method

This method, unlike the Brinell method, takes the permanent indentation depth as a measure of hardness. A steel ball indenter with a diameter of: $D = 1/16''$, $1/8''$, $1/4''$ or $1/2''$, or a conical diamond indenter with a cone angle of 120° and a spherical tip $r = 0.2$ mm can both be used, depending on the type of material whose hardness is measured. The magnitude of the indentation force is also selected based on the type of material, which allows the application of many procedures that are in use today. The most commonly used procedures are the first group of HRB and HRC. In the HRB method, a steel ball with a diameter of $1/16''$ is an indenter, which is pushed into the material with a force of 100 daN (**Fig. 5(a)**). If the indenter is conical and the indenting force is 150 daN then it is the HRC method (**Fig. 5(b)**). The HRC method is used for hard materials and the HRB method for softer materials (*Majstorović and Đukić, 1986*).

The procedure for determining hardness consists of three phases (**Fig. 5**). In the first phase, the material is acted upon with a force of 10 daN, whereby the indenter penetrates to a depth h_0 . This phase is performed in order to eliminate the influence of the surface layers of the material because, according to this method, the surface of the sample does not have to be specially prepared. In the second phase, the main force acts on the material, which in the case of the HRB method is 90 daN, and 140 daN for the HRC method. In the third phase, unloading is performed, whereby elastic deformations disappear and only plastic (permanent) deformations are retained (*Czichos et al., 2006*).

Rockwell hardness in the case of the conical indenter is described by the formula: $HRC = 100 - h_3/0.002$, while for the ball indenter it would be: $HRB = 130 - h_3/0.002$. The measure of hardness is the depth of indentation, expressed in Rockwell units, where the permanent indentation depth of 0.002 mm is equal to one Rockwell unit. The distance between the indentation centers, as well as the distance from the edge of the sample, should be greater than 3 mm. The measurement surface must be finely ground and clean, and perpendicular to the load axis (*Herrmann, 2011*).

Experiments have shown that it is much more convenient to measure hardness by the Rockwell method when the indenter is a cone. Only a small number of ceramics and CMCs can withstand the Rockwell test, which uses a total load of 60 daN, (HRA) while

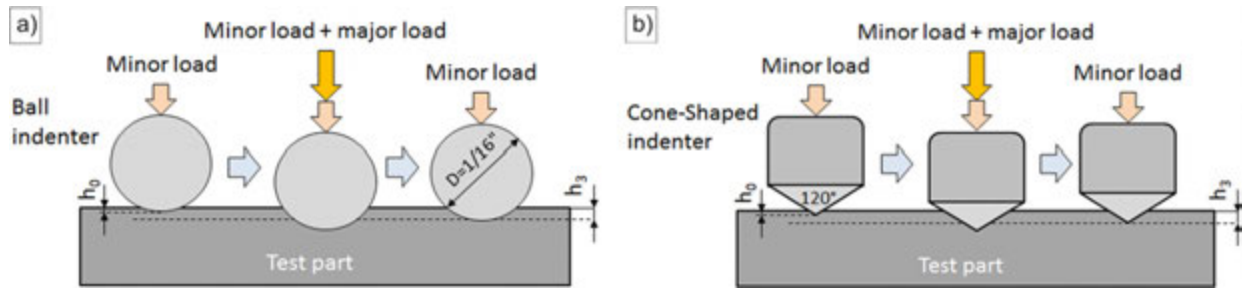


Fig. 5 Rockwell hardness measurement concept: (a) HRB method, (b) HRC method.

most ceramics can withstand Rockwell N test (N-scale) when the total load is 45 daN, 30 daN or 15 daN (respectively HR45N, HR30N and HR15N) (Kim and Kim, 2002). However, in the case of ceramics and CMCs, as extremely hard materials, this method is not very convenient (Clinton and Morrell, 1987).

The Knoop Method

The measure of Knoop hardness is the ratio of the indenting force and the surface of the indentation left by a pyramid diamond indenter with a rhombus base with angles α and β between opposite sides which are 172.5° and 130° in regards to the longitudinal axis of the indenter (Fig. 6).

Knoop microhardness is based on the equation:

$$HK = 1,451 \frac{F}{d^2} \quad (3)$$

where: F [N] - applied indenting force, and d [mm] - measured size of the longer diagonal of the indentation.

When testing the microhardness according to Knoop, there is a deltoid-shaped indentation, with the ratio of the sides being 1:30, which enables far more accurate measurement of the indentation diagonal. The indentation depth itself is smaller, so this method can be used to test very thin samples. The obtained results cannot be compared with the results from the Vickers microhardness test. Microhardness tests (Vickers, Knoop) use less than 1 daN loads for indenting and are usually performed on different devices. The advantage of microhardness is the possibility to measure the hardness at locations with different microstructures and in doing so measuring the hardness of individual phases. The main disadvantage is that the optical accuracy of the measurement becomes reduced due to resolution limitations (Czichos *et al.*, 2006).

There are usually two types of indentations available, from the Vickers pyramid and the Knoop pyramid. The Vickers indentation is a square with approximately equal diagonals and the Knoop indentation has different diagonals, where the longer diagonal is about 7 times longer than the short diagonal (Ben Ghorbal *et al.*, 2017). When these microhardness tests are used for ceramics, cracks at the corners around the indentations are less of a problem than with macro hardness tests (Fig. 7). However, the lower the load, the smaller the indentation is in the material, so it becomes difficult to accurately measure lengths (Clinton and Morrell, 1987).

Microstructural characteristics such as porosity, grain boundaries and secondary phases have a very important role in determining the indentation size, not only because of their own properties, but also because of their spatial distributions. High pressure at the indentation site in the presence of porosity can lead to the formation of larger indentations due to elimination of porosity. To reduce the error, the number of tests must be increased from the typical 5 for the macrohardness test to 10 or more for the microhardness test (Clinton and Morrell, 1987).

The Berkovich Method

The Berkovich method is based on pressing a regular three-sided pyramid into the material, whose hardness is being measured. Each edge of the pyramid makes an angle of 65.3° (Fig. 8) with the axis. Although it does not leave the smallest indentation, this indenter is used for the smallest loads for the nano- and pico-indentation. Since the indentation is not what is measured, but the displacement of the indenter, its size is not relevant. Berkovich indenter is used due to the highest precision of the tip geometry. Shallow penetration depths can be achieved by using instrumental nano-indentation ($h < 200$ nm) (Zivic *et al.*, 2012b). In this process, the tip of the indenter is pressed into the material with a variable force. The force is first increased to some maximum value of F_{max} , then unloading is performed until partial or complete relaxation of the material. During the indentation, the value of penetration depth at the applied force is measured and thus the load-unload curve is obtained. The depths achieved at certain moments of indentation are: h_m -maximum depth, h_c -contact depth and h_f -final indentation depth.

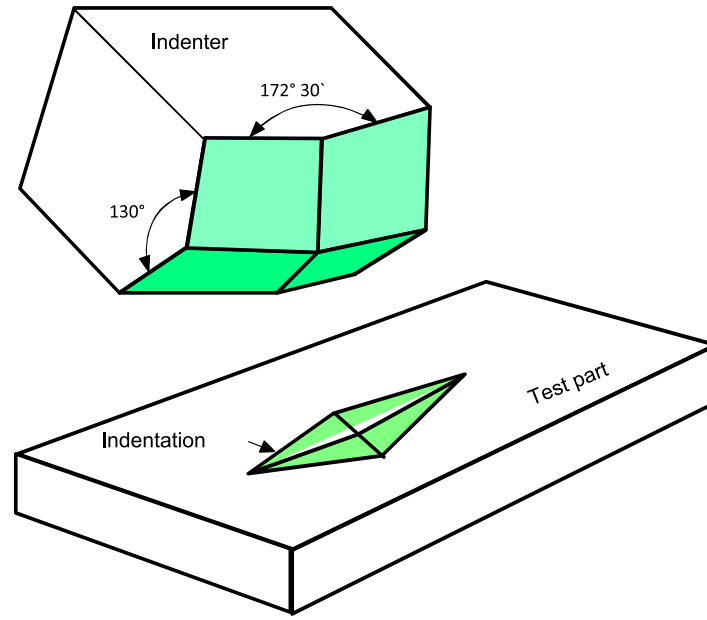


Fig. 6 Knoop hardness measurement concept.

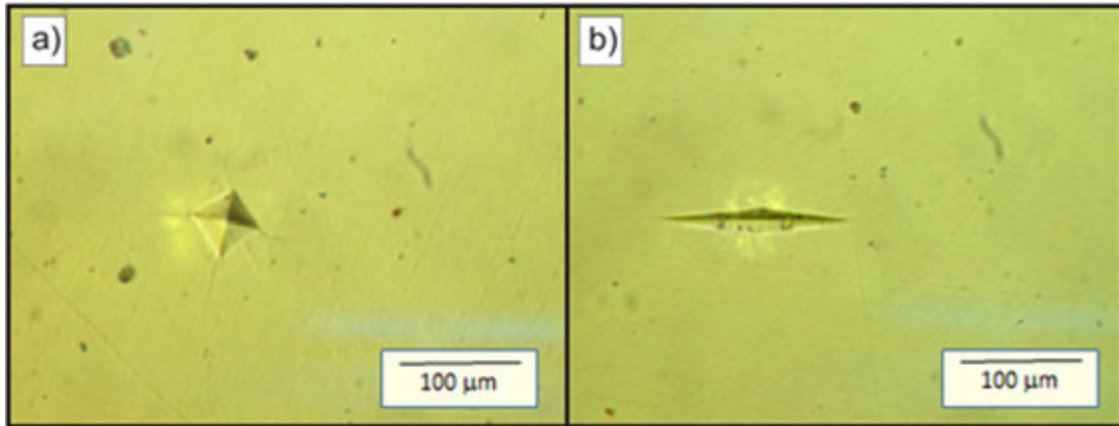


Fig. 7 Residual indent made at 0.5 daN load: (a) Vickers method ($HV_{0.5}$); (b) Knoop method ($HK_{0.5}$).

For the nano-indentation, indentation is not measured, like for the conventional processes, rather the hardness is determined directly based on the load-unload curve (Czichos *et al.*, 2006). Hardness (H) is determined by the following formula:

$$H = F_{max}/A \quad (4)$$

where: F_{max} - maximum force, A - projection of the contact surface, where ($A = 3\sqrt{3} h_c^2 \tan^2 \alpha$).

The given equations imply a perfect geometry of the indenter, however, each indenter has a rounded tip which is taken into account by extending these equations. In extended equations, numerous constants appear that describe the deviations from a perfect geometry, which is rather complex to determine. The projection of the contact surface is determined directly from the contact depth h_c , which is numerically determined from the load-unload curve, without measuring the indentation (Fischer-Cripps, 2007). Also, there are simplified new procedures for determining hardness. One such method is similar to the aforementioned procedure, with the difference related to determining the depth h_c , which does not require the calculation of contact stiffness and correction factors (Broitman, 2017). According to this procedure, the depth of penetration is determined can be based on the following Eqs. (5) and (6).

$$H_c = h_m - h_s \quad (5)$$

$$h_s = \eta(h_m - h_f) \quad (6)$$

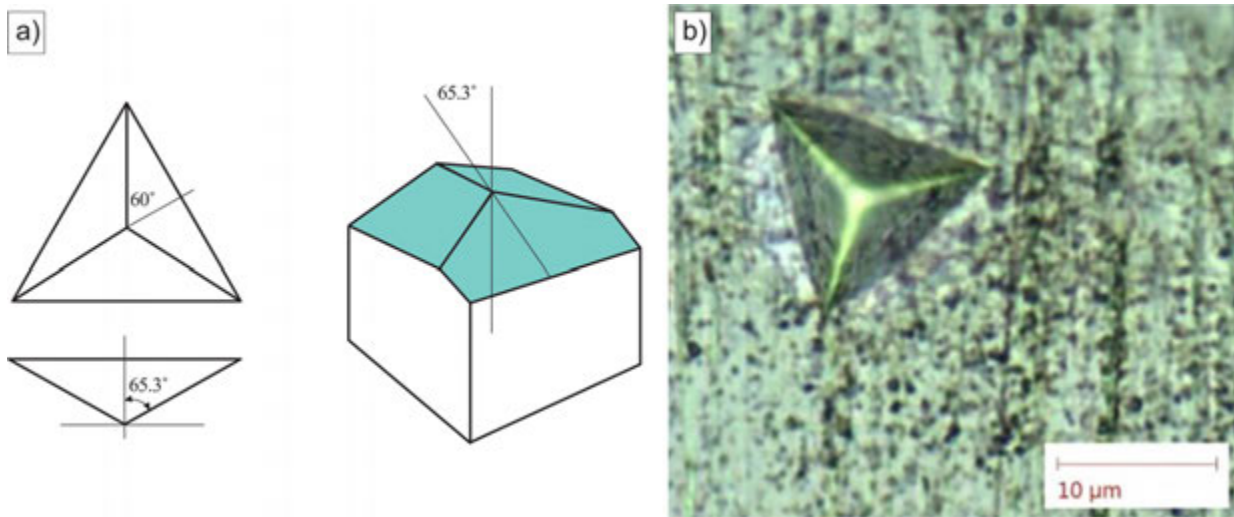


Fig. 8 Geometry and shape of the indenter in Berkovich method (a) and residual (b).

where, h_s is the elastic displacement of the surface; η is the geometric constant, which has a value of 0.58 for the Berkovich indenter.

In this procedure, the results are obtained quickly and easily, the contact depth h_c is determined quite simply, based on the measured maximum depth and the indentation depth after unloading. The equipment for this method consists of a computerized loading device that records the load necessary for indentation F in mN and the indentation displacement h in micrometers or nanometers (Shi *et al.*, 2019). Instead of the direct measurements of indentation size, which require optical microscopes, contact areas are calculated from depth measurements, for different shapes of the indenter. This is unlike procedures used for macro indentation tests, where lateral dimensions are used for calculating microhardness and macrohardness (diagonals for Vickers and Knoop tests, and diameter for Brinell test), instead of the permanent indentation depth. Hardness measurement errors can appear from different reasons, like:

- Incorrect calibration of optical magnification,
- Optical resolution limitations,
- Contrast and brightness limitations,
- Non-ideal geometry of the indenter,
- Existence of operator bias.

In macro indentation tests, the indentation is usually large enough for optical use. Displacement of insufficiently fixed or poorly placed samples during measurement gives incorrect hardness values. The presence of different impurities within the test module or external vibrations can cause displacements and lead to incorrect hardness values. For sensitive nanohardness measurements, even changes in room temperature can significantly affect the results (Peng *et al.*, 2004). The geometry of the samples also has an effect on the readings of hardness values: thinner samples give a higher apparent hardness, while measurement near the edge of the sample gives a lower value (edge effect). The main requirement in nano-indentations is that the surface is flat, parallel and undamaged, and both the measurement and the bottom surface have to be clean in order to avoid sliding. Rough surfaces lead to a large scatter of results (Elssner, 1999). External and internal porosity can interfere with measurements, especially if the tip falls directly into a large pore. The porosity of ceramics is related to mechanical properties (McColm, 1990), thus the reduction of porosity leads to hardness increase. Cracking around the indentation can change the shape and precision of the indentation, especially for coarse-grained samples, where the grains may split and separate (Carter and Norton, 2007). Although measurement errors can be caused by the physical morphology of the sample and its preparation, the largest source of error results from the uncertainty of diagonal length measurements, and equipment calibration, inadequate magnification power, human error, and poor image quality what can make the analysis of results inconclusive.

Nanoindentation has become one of the promising techniques in mechanical characterization of composites. However, size effects of different phases in composites must be considered, in order to perform appropriate nanoindentation (Abando *et al.*, 2021; Maiti *et al.*, 2018; Besharatloo *et al.*, 2019). Nanomechanical properties of the composite include complex theoretical considerations that depend on the composite nature, as well as its final applications. Many authors have recently used nanoindentation for characterization of CMCs, and one such review related to nanoindentation of composites is given in (Gautham and Sasmal, 2019; Pacheco-Torgal and Jalali, 2011; Angker and Swain, 2006). Nanoindentation of ZrB_2 ceramic composites showed that interphase properties have significant influence on the mechanical properties of the composite, and also provided some valuable insights into toughening mechanisms (Nayebi *et al.*, 2021; Shahedi Asl *et al.*, 2019). Nanoindentation can introduce controlled cracks and enable studies of crack deflection, and bridging at fiber/matrix interphase, and pull-out behavior (Xia *et al.*,

2004). This technique represents one of the methods to determine mechanical behavior of novel CMCs, like those including carbon nanotubes (Rivero-Antúñez *et al.*, 2020) or new glass composites (Amorós *et al.*, 2020). Even though this method is widely used, some aspects of testing results reliability are still under study (Besharatloo *et al.*, 2019).

Non-Destructive Testing (NDT) Methods for CMCs

Non-destructive testing (NDT) is a method of testing materials and components without damaging or destroying them. It is suitable in cases where the test sample should remain intact, especially in cases of high-responsibility parts when 100% control need to be performed and in cases of parts with expensive production processes that justify NDT in terms of cost (Prakash, 2012). Detecting defects in this way can be very useful for optimizing and improving the production process by analyzing the materials and quality of manufactured components. Commonly used destructive test methods generally provide more reliable data, but test samples are destroyed during the test what makes this type of test more expensive than NDT. These aspects are particularly interesting for ceramic matrix composites (CMCs). The production of CMC components involves high production costs, thus justifying the use of NDT. Most CMC components are used in highly critical environments, which require 100% integrity assurance (Rawlings, 2009). NDT methods can detect typical defects, such as cracks, delamination, inhomogeneities, pores or inclusions (Vaara and Leinonen, 2012). Some of the traditional NDT methods that can be used to detect CMC defects are:

- Visual and haptic analysis,
- Acoustic emission method,
- Ultrasound analysis,
- Penetration method,
- Thermographic/infrared (IR) analysis,
- Radiography and
- X-ray computed tomography (CT).

None of these methods is universal nor fully meets all the requirements. Each method has an area of application and a range where it has the highest efficiency (Krenkel, 2008).

Visual and Haptic Method

The most basic and often underestimated NDT methods are based on fundamental human senses. These include visual, tactile (haptic) geometric analysis. Modern NDT methods improve the human senses with mechanical and computer aids, enabling a faster and more reliable testing method. For example, specially designed computer algorithms can quickly identify defects by comparing non-damaged samples and predefined damage criteria, faster and more reliably than humans can (Abando *et al.*, 2021). Visual inspection is a key NDT method that is present in all production processes involving human interaction. Certain quality control systems can be performed using fully automated computer methods of visual inspection. With precisely formulated algorithms, computers can perform quality control which is why computer automated systems are used in a large number of different production processes (Wang *et al.*, 2020). The basic use of a computer-aided visual NDT consists of a digital camera that photographs the samples and compares the obtained images with the reference sample. For example, ceramic tiles can be tested for geometric imperfections such as distorted surfaces, cracks or missing pieces.

Similar to visual inspection, detection of surface deformation by touch can be used to detect variations in surface structure. Automated systems are based on direct contact systems, such as geometric analyzers or laser interference systems that scan the surface topology of the sample. Computer-aided methods compare the obtained data with the existing reference sample data and decide if the sample is good or false, depending on whether the data is within or outside the defined specifications (Hausherr *et al.*, 2009). Examples of computer-aided haptic NDT are laser topographic systems that determine external geometric dimensions.

3D scanning systems are evolving due to development of composites by novel additive manufacturing that is based on computer processing of layers and 3D elements in simulation of the material structure (Zhao *et al.*, 2021; Jia *et al.*, 2021). Accuracy of 3D measuring systems is influenced by many aspects of composite structure, surface quality and complexity of shapes, as well as software processing (Kurz *et al.*, 2015). Additionally, software algorithms related to image processing are complex and still under development (Bartoszek, 2020; Huñady and Hagara, 2017; Zhao and Rosen, 2017).

Acoustic Emission Method

The sound-based method known as the acoustic emission method is increasingly used in the evaluation of the structure integrity, usually based on fracture mechanics. The method allows dynamic monitoring of defect behavior under stress. The test sample is subjected to stress, mechanical or thermal, that is usually slightly higher than the maximum working stress. Under load, the cracks open and release energy in elastic waves. These waves are registered by the acoustic receiver and enable monitoring of crack growth

under load, which provides important information on the material resistance to fracture, and by triangulation, it is possible to find the position of the defect. The method is very sensitive and can monitor large surface with a single receiver (Wang *et al.*, 2020).

Acoustic emission has found wide application in determining the overall component state at some load. Namely, during the crack initiation, or crack propagation, relaxation of the accumulated internal energy occurs in the material in the most loaded places (e.g., flow of the material). Part of the released energy is converted into short high-frequency sound impulses, which are detected and converted into electrical impulses (signals) by the appropriate probes located on the sample surface. The network of detectors is placed on the surface of the sample and, by monitoring the time of arrival or delay of the generated impulse to the detector, the location of the crack or the zone of crack initiation can be determined. The amplitude of the produced impulses can give a direct correlation with the energy created by the change in the material density. For the correct interpretation of the test results, experience in results interpretation is necessary, because high-frequency sound impulses can be partially lost or transformed, when passing through the material (Mix, 2005). In addition, the construction components, loaded during operation, also create their own noise, which need to be separated from the relaxation energy generated by the elasto-plastic material deformation (Bansal and Lamon, 2015).

Ultrasonic Method

Ultrasound analysis was developed mid last century (Szewieczek and Hillger, 2009). After successful application in medical research and diagnostics, the procedure was adapted for material research. It has been developed into one of the most reliable non-destructive testing methods available and widely used today. This method can reliably detect pores, inclusions, cracks and delamination in the CMCs (Wu *et al.*, 2019; Im *et al.*, 2019; Jhang, 2009; Cannata *et al.*, 2006; Kim *et al.*, 2020). Ultrasound analysis is based on the partial reflection of the high-frequency ultrasound signals (50 kHz–200 MHz) when encountering a change in density. This method detects changes in density within the sample, thus it can be used for the detection of all damage types based on density change, such as delamination, cracks, pores or inclusions (Hausherr *et al.*, 2009). At higher wavelengths, the test sensitivity, especially for small defects, decreases sharply, and at frequencies higher than 10 MHz, strong damping occurs at the grain boundaries, so the propagation of ultrasonic waves is difficult. The three most common ultrasound analysis methods are (Fig. 9):

- Echo – pulse method,
- Transmission method,
- Phased array ultrasonic testing.

Echo-Pulse Method

The echo-pulse method is based on the change of the density gradient. Instead of measuring the signal passing through the sample, echo-pulse analysis observes the acoustic energy reflected inside the sample, and returning again to the sample surface. The advantage of this method is that both the emitter and the receiver are located on one side of the sample, which enables the scanning of complex and closed constructions such as pipes or constructions with irregular topology. Another advantage is the ability to detect the depth of damaged areas. Knowing the speed of sound, damage zone within the sample can be calculated by measuring the time that passes between the emission and the return of the signal (Wang *et al.*, 2020). Fig. 9(a) shows the schematic diagram of the echo-pulse method.

Performing this method takes much longer than other methods (a typical measurement of a 300 × 300 mm plate requires approximately 10 min) and there are rather small sensitivity to detecting defects in objects with a complex shapes. However, this method is considered as quite sensitive. It is considered that only 5% of sound energy is reflected due to inhomogeneity in the material. The drawback of this method is the so-called ‘dead zones’. At the point of entry of the ultrasound into the material, the emitted impulses cannot have a small enough length to immediately detect defects near the ultrasonic head (Prakash, 2012). By using ultrasonic damping, this zone can be significantly reduced to only about 5 mm. The surfaces of sound intrusion and reflection should be parallel and smooth.

Transmission Method

The transmission method is similar to the previous one, with the difference being that it uses two separate probes, one that only emits impulses and the other, located on the opposite side of the test object, serves as a receiver of the impulse passing through the material (Fig. 9(b)). If the ultrasound impulses encounter a defect on their way, they will be partially reflected, depending on the size and character of that defect, and a reduced amount of energy will continue the path to the receiving probe. The defect reads as a lower signal height or, in the case of a larger defect, as the absence of a signal on the device screen (Abando *et al.*, 2021). Modern devices are made for testing having both of the previously listed techniques.

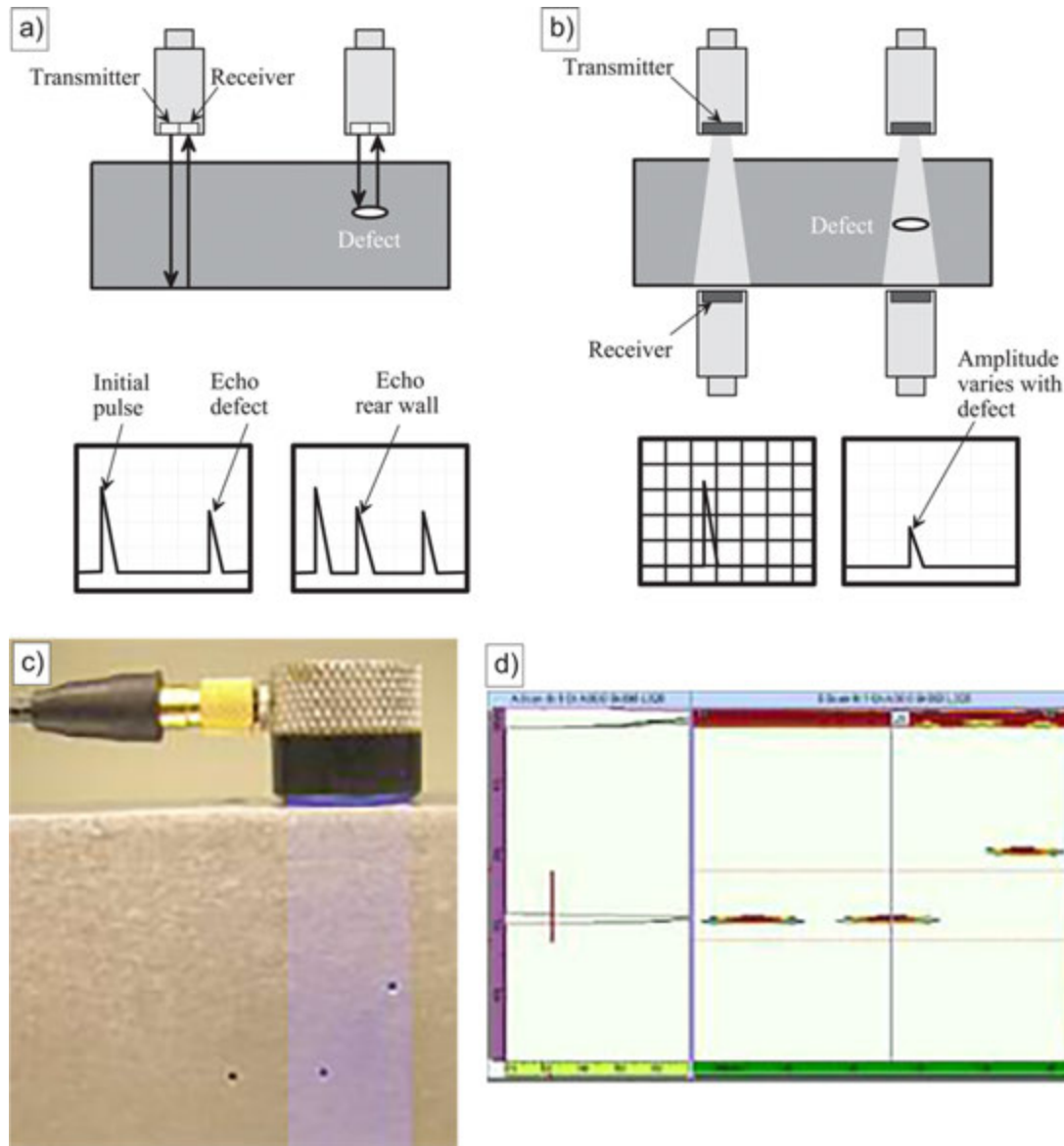


Fig. 9 Echo-pulse method (a), Transmission method (b), Phased array ultrasonic method (c).

Phased Array Ultrasonic Testing

The Phased array (PA) method is an advanced method of ultrasound testing that was initially used in medicine but has since found application in engineering. It is commonly used for finding defects in various materials. Single-element probes, technically known as monolithic probes, emit a beam in a fixed direction. To inspect or test a large amount of material, a conventional probe must physically move (scan) to test the area of interest. In contrast, the beam of phase array probes can be focused and moved electronically without moving the probe. Ultrasound can be controlled due to the phase array probe being composed of several small elements, each of which can be programmed individually over time. Ultrasonic testing with a phase array method is based on the principles of wave physics, which is also used in areas such as optics and electromagnetic antennas (Strand, 2008).

The PA probe consists of many small ultrasonic transducers, each of which can pulse independently. By changing the time, for example by progressively moving the impulse from each transducer in a certain direction, a constructive interference pattern is set which results in the ultrasonic wave emission at a set angle depending on the progressive time delay (Vaara and Leinonen, 2012). In other words, by changing the progressive time delay, the beam can be controlled electronically, thus cover a larger area of the tested material, while data from multiple beams is coherently compiled to create a visual image showing a cross-section of the test object (Fig. 9(c)).

Most ultrasound analyzers require the sample to be immersed in water. When performing air tests, due to the large reflection on the air-material density gradient, the received signal strength is extremely low, which makes ultrasound analysis in air difficult

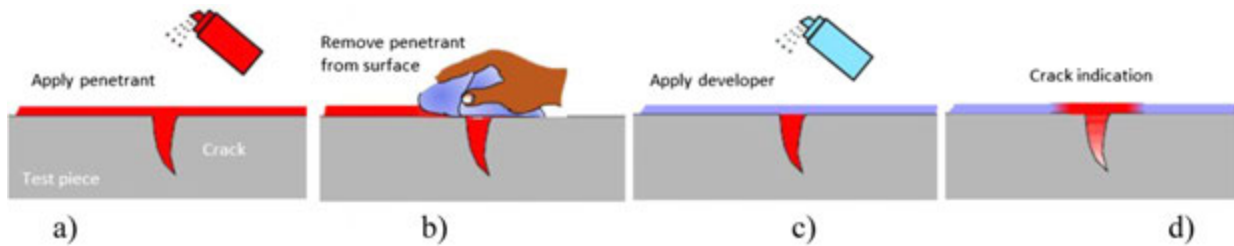


Fig. 10 Procedure for performing the penetrant method.

(Prakash, 2012) (Hausherr *et al.*, 2009). The solution is to analyze a sample immersed in water and thus increase the signal strength. However, this is a problem for water-sensitive materials, such as highly porous structures or objects made of water-soluble materials. This problem was solved in the late 1990s with the development of new ultrasound analyzers (Mix, 2005).

Penetrant Inspection

Penetrant methods of defectoscopy (capillary defectoscopy methods) are based on the fact that liquids with high capillary activity, called penetrants, are drawn into very narrow, invisible cracks on the surface of the material and cavities connected to the surface. After removing the excess liquid from the surface, defects can be visible in a daylight or ultraviolet light. For this purpose a developer, a powder or suspension is applied to the material surface, which draws the surfactant out of the cracks and cavities by capillary action. These methods rapidly developed in recent years as a result of the efforts to find simple and effective ways of detecting surface defects or subsurface defects connected with the surface in non-magnetic materials and in non-metals (Prakash, 2012). Due to their simplicity, they have become widespread for both magnetic and non-magnetic materials in many sectors of industry and exploitation.

The concept of penetrant testing is shown in Fig. 10. The test surface is covered with penetrating liquid by immersion, spraying or brush application (Fig. 10(a)). After a period of penetration (which, depending on the type of penetrant, the temperature, the surface and tested material, is 2–30 min), the surface of the test object is wiped down well or washed and dried (Fig. 10(b)), and then the developer (dry or wet) is applied on it (Fig. 10(c)). Penetrant left in cracks and cavities enters the developer due to capillarity and shows up in a visible or ultraviolet light, since it contains paint or fluorescent matter (Fig. 10(d)) (Abando *et al.*, 2021).

Penetrant testing has many advantages over other non-destructive testing methods, the biggest of which is that testing equipment is relatively inexpensive, easily portable and very easy to perform with. The applicability of penetration methods is limited to the detection of surface and subsurface defects that are connected to the surface. In addition, surfaces tested with these methods have to be relatively smooth and clean. The speed of testing by these methods and their efficiency depends on the surface and ambient temperature. Interpretation of the results obtained by penetrant defectoscopy is very simple (Mix, 2005).

Thermography

Compared to ultrasound analysis, thermographic analysis is a passive system that detects defects by analyzing temperature changes (Kordatos *et al.*, 2012). Thermographic analysis is based on the detection of infrared energy radiating from an object, mainly in the range of 3–5 μm , using specially adapted infrared detectors. Usually, the heat radiated from the surface of the structure is constant and does not change over time (Khattak *et al.*, 2016). There are two basic options for performing infrared thermography, the passive and active approach. If an object is recorded in a steady (stationary) temperature state, which is achieved by keeping that object in a constant temperature environment for some time, that is passive thermography. If the radiation emitted from the surface of the object is different from the radiation emitted by its surroundings, it will be visible on the thermogram (Mix, 2005).

Thermal imaging (infrared photography) is a non-contact passive NDT method of measuring temperature and its distribution on the object's surface by registering infrared radiation emitted by an object and using an IR camera to convert it into a visible image in the form of a temperature field. This requires the object to have a temperature difference to the outside temperature and an internal heat pressure on the surface of the object (Hausherr *et al.*, 2009). The amount of infrared energy radiated from the surface of an object depends on the geometric and material properties, resulting in a unique heat signature that is detected by an infrared camera. The advantage of thermal analysis is its ability to monitor in-situ, and during operation. Passive objects without internal heat effect cannot be analyzed by this method, therefore it is required that the object has its own heat source (Hausherr *et al.*, 2009). The most important requirement for obtaining relevant and practical results using the IR thermography is the existence of a temperature difference or thermal contrast ΔT between the internal defect in the observed object and its environment. When the stated requirement is not already met, and need to be achieved, that is active thermography (Meola *et al.*, 2017).

Active IR thermography is a measurement technique, which is used when the observed object is at the same temperature as the environment, or if the properties below object's surface are observed. It is generally accepted that active thermography is any IR

measurement technique that requires additional thermal stimulation of the object being observed in order to achieve the required temperature difference (Meyendorf *et al.*, 2013). In order for active thermography to give usable results, it is necessary to introduce an additional requirement. Namely, the thermophysical properties of internal defects must be different from the thermophysical properties of the object's material itself. The detection of defects within the observed object is not possible if this requirement is not met. There are several active thermography techniques that can be used in non-destructive testing, which differ in the thermal stimulation of the observed object, the method of data collection and processing:

- Step-Heating (SH) Thermography,
- Vibrothermography (VT),
- Pulsed Thermography (PT),
- Lock-in Thermography (LT),
- Pulsed Phase Thermography (PPT).

There is a wide range of energy sources used to excite the temperature contrast between the damaged and undamaged area in the observed object. They can be divided into *external sources* (in case the energy is transferred to the object's surface, and then transmitted through it until it reaches a defect) and *internal sources* when energy is introduced into the observed object to stimulate only the defect. External sources are standard optical devices such as xenon flashes or halogen lamps, while mechanical sound oscillations or ultrasonic source are used as internal stimulation (Meola *et al.*, 2017).

Step-heating thermography (SH) is a technique of active thermography in which the object surface temperature growth is measured in time steps, while continuously exciting the temperature difference by prolonged heating with a weak heat source (Maldague, 2000). The measurement of temperature change is not limited to the heating period, it can also be done after the heating has stopped. The evolution of the surface temperature of an object over time depends on the thermal diffusivity within the structure of the object itself, which depends on whether there are defects on the inside (Balageas and Roche, 2014). Materials with lower thermal conductivity and thermal diffusivity, as well as objects with deeper defects, can be tested by using the SH technique. The advantage is the low speed required for collecting (recording) thermograms, as well as the low cost of the required heat sources (IR or halogen lamps). The disadvantage is the difficulty of uniform heating of the entire object surface (Roche and Balageas, 2014).

Pulsed thermography (PT) is a technique in which the observed object is thermally excited by short thermal impulses coming from several lamps (flash lamps) that ensure instantaneous heating of the target object (Fig. 11). Infrared cameras monitor the temperature on the object surface. In order to get a better thermographic image by depth, the lamps are placed at certain distances from a few millimeters to several meters. It is used for materials with high thermal conductivity (impulse duration up to several milliseconds), while for materials with lower thermal conductivity it is necessary to keep the heat impulse for a few seconds. The measurement procedure using the PT technique consists of heating the observed object with a heat impulse, and then observing the cooling curve (Meola *et al.*, 2017). Qualitatively, the PT measurement procedure can be described by the temperature of the material changing rapidly after the initial heat impulse, because the thermal front progresses by the mechanism of thermal diffusivity (a measure of the rate of heat travel through the material). Radiation losses affect the advancing of the front. The existence of defects in the observed object changes the thermal diffusivity, so object's surface temperature is different from the ambient temperature at the location above the defect (Chen, 2007). Since the heat impulse (wave), needs some time to penetrate to a certain depth in the material, the recording time after the wave is sent gives information about the depth level. The advantage of pulsed thermography is data about different depths from a series of thermograms taken after sending a single impulse. However, pulsed thermography is not suitable for measuring very weak temperature signals.

Vibrothermography (VT) is an active thermography technique that uses the effect of heat released due to friction caused by mechanical vibrations (0–25 kHz) induced on the surface of the observed object (Chen, 2007). While ultrasonic waves travel

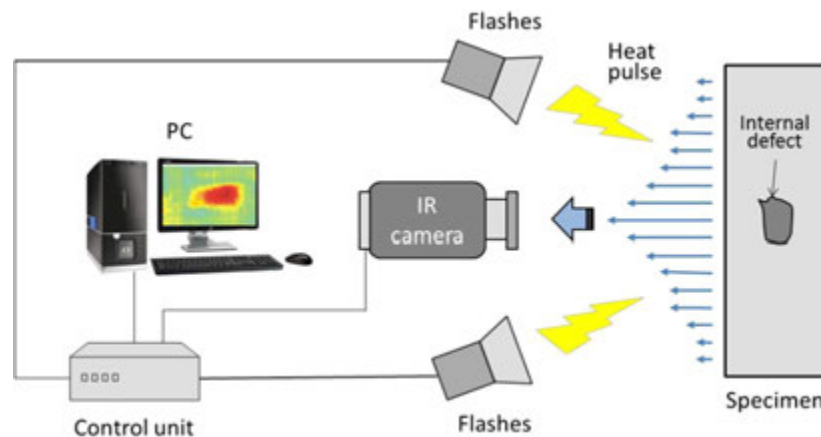


Fig. 11 Schematic representation of pulsed thermography.

through a homogeneous material, heat is released at the site of defects such as cracks (Fig. 12). Periodic waves cause an increase in temperature at the places of stress concentration. This method is also called Ultrasonic induced thermography. The main advantage of Vibrothermography is the ability to detect small cracks. Instead of blocking externally induced heat waves, ultrasonic excitation allows the defect itself to become a heat source. The amplitude and frequency of the excitation can be modulated according to the frequency spectrum of the ultrasound for a certain application (Li *et al.*, 2017).

Lock-in Thermography (LT) uses similar elements and testing equipment as Pulsed thermography. The difference being that the signal generator sends oscillating sinusoidal thermal waves (sinusoidal modulation of the heating lamp), instead of unit impulses, where the heat is sent periodically with a constant frequency (lock-in frequency) (Meola *et al.*, 2017). The sinusoidal shape corresponds to intensity (from the highest to the lowest amplitude), which actually represents the heat sent and returned from the object recorded by the infrared camera. When the input wave penetrates the surface of the material, it is absorbed and shifts phases. When the input wave reaches the area inside the object with certain defects, it is partially reflected. This reflected wave interferes with the incoming wave which creates a different surface temperature pattern (Fig. 13). Finally, the defect depth can be determined by estimating the phase shift of surface temperatures relative to the input wave. The lower the frequency of the input wave, the more information is obtained about the depth levels of the material or object. The optimal frequency depends on the thermophysical characteristics of the material, as well as its thickness. The type of tested material (thermal diffusivity), determine the depth to which it is possible to detect defects (Busse, 2014). The advantage of this type of thermography is higher sensitivity and better thermograms of materials for complex structures. Unlike Pulsed thermography, the Lock-in method requires significantly longer measurement times and several measurements to obtain defect depth data (Chen, 2007).

Pulsed Phase Thermography (PPT) is a technique in which the collected data is transformed from time domains into frequency domains using one-dimensional discrete Fourier transform (DFT) (Ibarra-Castanedo and Maldague, 2004). The PPT technique is considered as crosslinked between the PT and LT techniques, since it combines the advantages of both of these techniques. Although not obvious, the

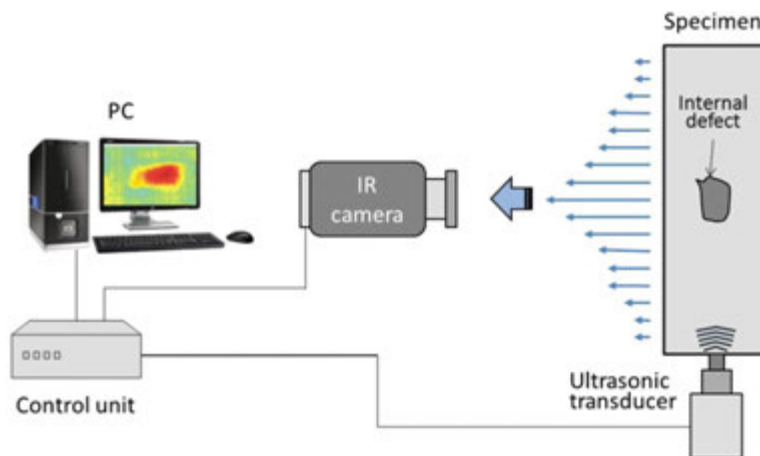


Fig. 12 Schematic representation of Vibrothermography.

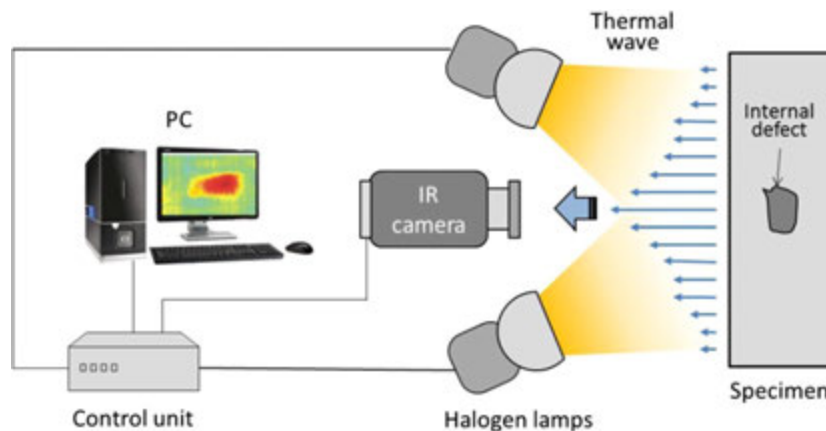


Fig. 13 Schematic representation of the Lock-in thermography.

link between PT and LT techniques can be established through the concept of superposition, i.e., the fact that each waveform, periodic or not, can be approximated by the sum of harmonic waves oscillating at different frequencies (Maldague *et al.*, 1997).

Radiography

Radiography is one of the most commonly-used methods for non-destructive testing (Maldague, 2000). Radiographic methods are mainly used to determine the homogeneity of different materials and their compounds. The X and γ rays, with very small wavelengths, used in this test, are partially absorbed when passing through hard materials. Since the human eye cannot detect X-rays, it is necessary to use an intermediate medium or measurement to make the radiation visible. This can be achieved in various ways, using chemical or physical effects (Prakash, 2012). Due to the differences in the basic principles, each method has certain advantages and disadvantages. The permanent image obtained by the action of radiation on a photographic emulsion is called a radiogram. The radiogram can be obtained on radiographically sensitive film, or paper, as well as on electrostatically sensitive material. Once developed and fixed, the image is stable and can be stored for archiving. The main drawback is the fact that the image cannot be seen "live". To see the results, the film must be developed by a chemical process that requires a few minutes. Incorrect X-ray parameters, such as voltage that is too high or too low, can make the image unusable, what is a common source of errors (Abando *et al.*, 2021). A limited-duration image is an image on fluorescent screens, which disappears when the radiation stops acting on the screen. The main advantage is the ability to view the live image and the subsequent ability to adjust the intensity of the X-rays, in order to obtain optimal contrast. Disadvantage is a low resolution (Wang *et al.*, 2020). The purpose of all methods of radiation control is to enable qualitative and quantitative monitoring of detected structural irregularities in the material's volume or in the cross-section of the tested material. Working with radiation sources requires special attention and training, and operators need professional trainings in these techniques, as well as in safety measures (Oruč and Sunulahpaši, 2012). Investigation of electromagnetic methods in NDT of composites is also very important (Wilson and Tian, 2007).

Concept of the Method

The radiation source is located on one side of the object, while on the opposite side, next to the object, a film is attached to register the passing radiation. Cavities representing defects are inscribed in the object, and the difference in thickness shows the influence of thickness on radiation absorption (Fig. 14). The radiation passing through the object is more absorbed in zones of higher density and thickness, causing a change in the radiation intensity. The change in the radiation intensity through the material, results in the irregularly distributed darkening of the film, and these differences in the level of darkness are called radiographic contrasts (Prakash, 2012).

The intensity of the transmitted radiation depends on the object thickness at the observed location and the absorption coefficient of the material through which the radiation passed. Irregularities expected in the object are most often voids, gas bubbles and inclusions. The intensity of radiation after passing through irregularities with lower density than the base material will be higher than the radiation intensity through the cross-section of the object without irregularities. In addition, any reduction in the thickness on the radiation path will also result in a higher intensity of the passing radiation. Accordingly the variable radiation will act on the film (Amorós *et al.*, 2020). Any defect that causes a decrease in absorption allows a local increase in radiation

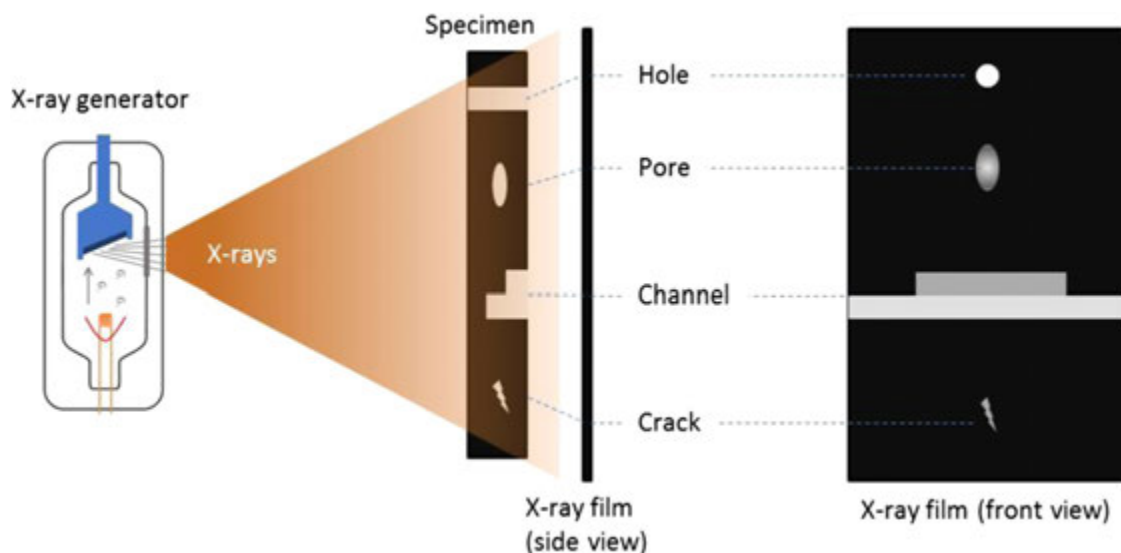


Fig. 14 Concept of producing radiograms.

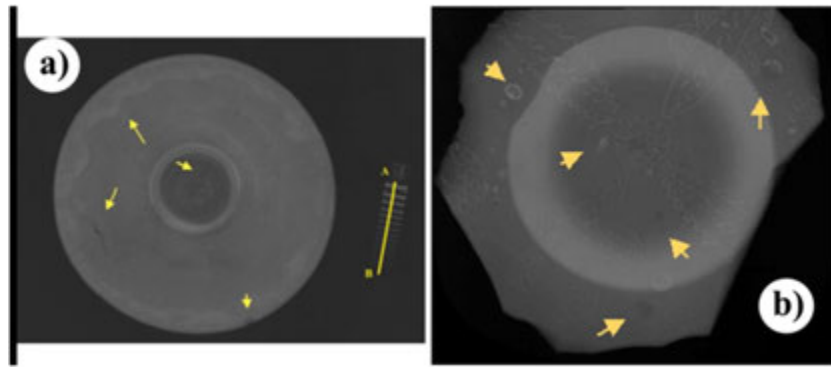


Fig. 15 Radiography images showing defects: (a) Ceramic antique bowl, (b) Ceramic antique plate. Images adapted from Negahdarzadeh, E., Yahaghi, E., Rokrok, B., Movafeghi, A., Keshavarz Khani, A., 2019. Diagnosis of design and defects in radiography of ceramic antique objects using the wavelet-domain hidden Markov models. *Journal of Cultural Heritage* 35, 56–63.

intensity, while metal inclusions of higher density than the base material reduce the radiation intensity. On the film, the higher intensity is manifested by more dark areas (Mix, 2005).

In CMCs, the matrix and reinforcing fibers have different densities, therefore causing different radiation damping, thus showing on the radiograph by different darkening. Defects such as pores or cracks will be visible as more dark areas. For ceramics, radiography is commonly used in dentistry, to provide radiographs of teeth (Van den Breemer *et al.*, 2021). Radiography is one of the established techniques in evaluation of ceramic antique objects, as shown in Fig. 15 (Negahdarzadeh *et al.*, 2019). In general, radiographic images are rather blur when focused on details at micro scale and their resolution is rather low. This is the satisfying quality for most of the medical applications, but in material research, especially in study of composite structures where micro- and nano-scale details are of the utmost importance, this resolution is not good enough. Different software processing of radiographic images has been studied as well (Negahdarzadeh *et al.*, 2019).

For example, radiographic image of the ceramic brake disc made of SiC matrix with short carbon fibers can point out zones with rich (dark gray areas) or reduced carbon content (light gray areas) (Hausherr *et al.*, 2009). In comparison to a reference sample, it is possible to estimate the absolute quantitative ratio of fibers and matrix, but this is not highly precise technique. Radiography is very useful for determining the inhomogeneity of materials such as pores, inclusions and other defects that are reflected in the difference in density. However, there are some types of defects that cannot be registered. Since radiographic analysis can only register the total attenuation of X-rays passing from the source to the detector, it is not possible to distinguish the localized attenuation in one or several thin layers, which makes it impossible to detect delamination.

Different attempts to improve traditional radiography have resulted in several new high-resolution X-ray and electron imaging, like Scanning Electron Microscope (SEM), Computed Tomography (CT), Magnetic resonance imaging (MRI), Transmission electron microscopes (TEM). However, increase of resolution significantly decreased the area of analysis (field of view), even down to nano-scales (TEM). Additionally, significant research area is related to development of in situ diagnostics. High-resolution diagnostics, especially in situ, are of the utmost importance in different applications, whereas the main driver is medical sector. In material science and composite development, such devices will bring opportunities for understanding many unresolved issues in development and functional use of advanced materials. In situ ultra-high-resolution at micro and nano scales is one of the state-of-the-art areas (Artyomov *et al.*, 2020; Faenov *et al.*, 2018; Chateau *et al.*, 2011). These devices are complex and currently evolving and generally belong to a microscopy group of devices. Microscopy represents very large field from aspect of existing devices, from traditional optical microscopes, to high resolution SEM and TEM microscopes. The scope of this article does not allow more detailed descriptions and there is a large scope of existing literature (Cho, 2020; Thomas, 2017; Kirkland, 2020; Santos and Carvalho, 2019; Lawlor, 2019; Hawkes and Spence, 2019). However, in development of advanced materials like composites, CT imaging is one of the unprecedented existing devices today and short concept is given further.

Computed Tomography (CT)

The main disadvantage of radiographic method was the lack of true 3D visualization when analyzing complex three-dimensional components and elements. 3D visualization was achieved by the introduction of computed tomography in the 1980s, based on development of powerful computers that could solve complex algorithms for describing 3D volume by using a series of 2D radiographic images (Abdul-Aziz, 2006). In this way, 3D visualization of the object from any angle or position was enabled, which has led to a new quality of material testing without destruction. The test sample does not need to be specially prepared and it is possible to detect defects of less than 1 μm (Strand, 2008). Since the procedure is based on X-ray attenuation, any irregularities that have a different density than the base material can be observed (Hausherr *et al.*, 2009).

There are two basic concepts of computed tomography, spiral and rotational. The spiral scanning system consists of the source and the X-ray detector rotating around the sample in a spiral path along the length of the sample. Very long objects can be

examined in this way. This system is used primarily in medical diagnostics. In a rotary computed tomography system, the X-ray source and the detector are stationary and the sample is placed on a turntable and rotated in small steps. This way, a sufficiently large number of 2D radiographic images can describe the 3D structure of any object, supported by the algorithms for mathematical reconstruction. Specialized visualization software can virtually show complete 3D internal structure throughout the whole volume with resolution depending on the hardware properties of the CT device. There are significant ongoing efforts to develop lower cost CT devices, also portable ones in order to enable wider application of these diagnostic methods (see “Relevant Websites section”). For research purposes in material science, micro-CT device was developed, with possibility to 3D scan small material samples, down to nano scales (Erdelyi *et al.*, 2020; Babcsan *et al.*, 2014).

Defects and damaged areas within the test sample, such as cracks or pores, usually consist of an air-insulated space that reduces X-ray attenuation. Defects and their dimensions are determined based on the detection of these local changes in attenuation. Defects such as cracks or pores are visible as areas of darker gray (Zou *et al.*, 2016). Although CMCs are heterogeneous materials that consist of a matrix and reinforcements made from different materials, the existence of pores and cracks, due to their significantly lower density, can be reliably detected. It is also possible to detect the existence of inhomogeneities in the matrix or fiber damage. Unlike radiography, computed tomography can also successfully detect defects in the form of delamination, since the examined part can be observed in different sections.

New direction in material characterization is in situ recording of data during the testing, like combination of CT scanning with tensile testing of SiC/SiC composites (Mazars *et al.*, 2017). This approach in material characterization can reveal aspects of dynamic processes that occur during certain load regimes, like damage mechanisms. X-ray CT scanning is extremely useful in composite characterization, because it can easily reveal defects like no other existing technology today, and this technology is becoming one of the mostly promising one in industrial quality control. It can be seen from Figs. 16 and 17 that CT scanning can provide internal structural details and profound knowledge on damage evolution, as well as forms of damage that can occur within a composite structure. 3D image provided by the CT scanning consists of multiple 2D images (CT slices) and the number of such 2D images in one 3D CT image depends on the initial resolution that is setup by the operator. More 2D images means more precise internal structure showed by the CT image, but it can be very time- and resource- consuming and optimum resolution depends on the application (functional requirements of the tested material). Fig. 16(a) shows how the change of resolution provides different level of material details (like cracks). Comparison of Fig. 16(b) and (c) shows the difference between CT image (possibility to see internal details of the structure without destroying it) and optical image (only surface image possible). CT scanning is very useful for determining damage types within a structure (fiber debonding, fiber failure, interphase shapes, etc.), as shown in Fig. 17.

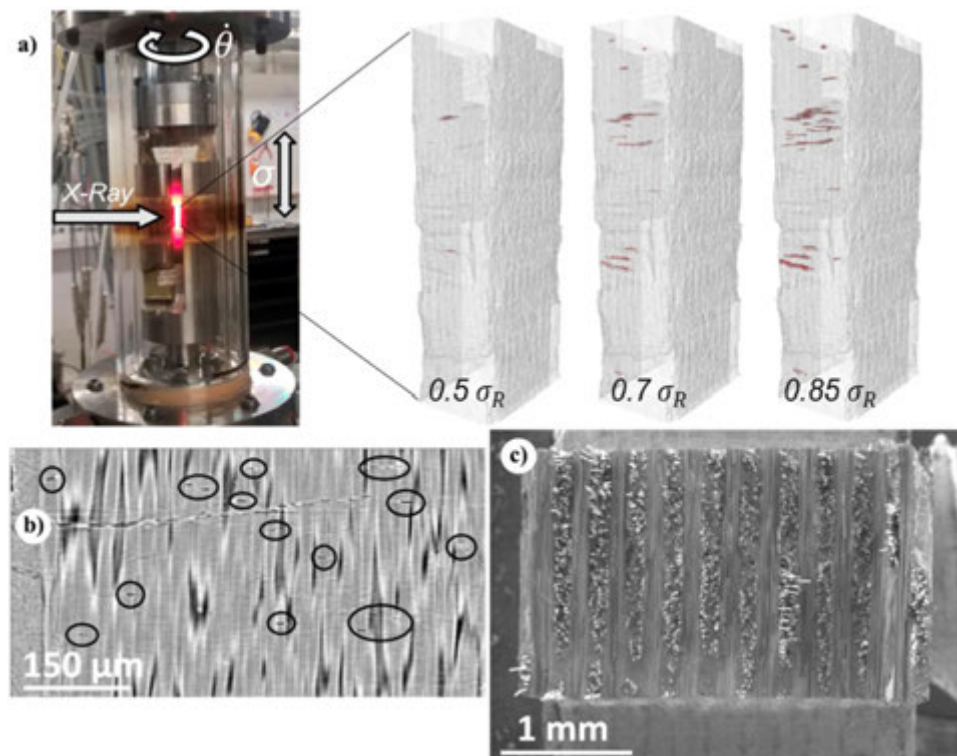


Fig. 16 CT images: (a) In situ testing of the composite fracture, with CT visualization (three different resolutions of CT scanning, showing cracks in composite structure); (b) CT slice showing cracks (transverse) in the composite structure (fiber failures); (c) optical image of the fracture composite surface. Images adapted from Mazars, V., Caty, O., Couégnat, G., *et al.*, 2017. Damage investigation and modeling of 3D woven ceramic matrix composites from X-ray tomography in-situ tensile tests. *Acta Materialia* 140, 130–139.

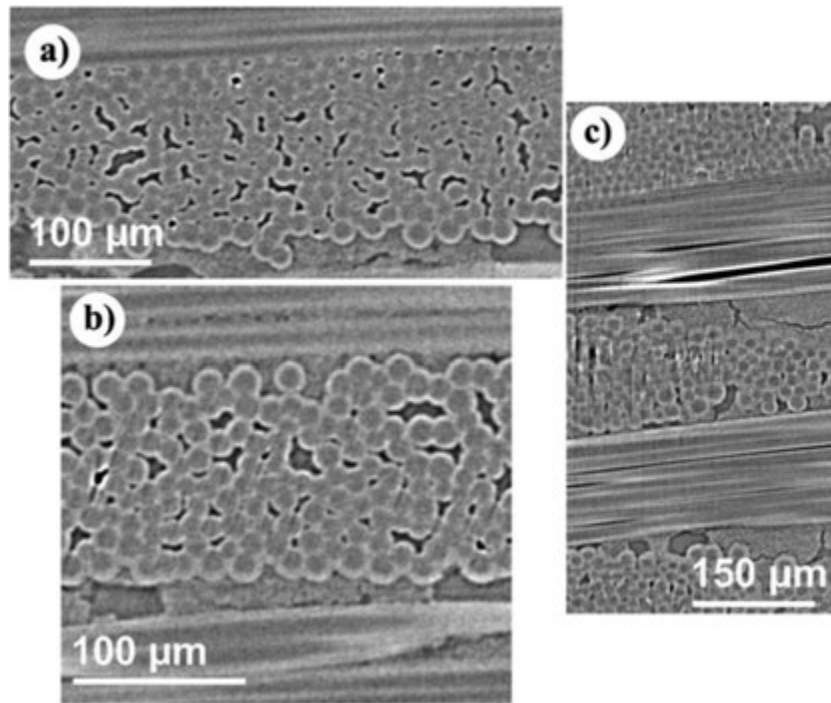


Fig. 17 Different CT slices showing internal voids and cracks in the composite structure: (a) debonding of the fibers; (b) failure of the fibers; (c) fiber/matrix composite structure. Images adapted from Mazars, V., Caty, O., Couégnat, G., *et al.*, 2017. Damage investigation and modeling of 3D woven ceramic matrix composites from X-ray tomography in-situ tensile tests. *Acta Materialia* 140, 130–139.

Three-dimensional observation of the entire volume enables morphological examinations, such as crack propagation and determination of phase distribution and porosity (Mazars *et al.*, 2017; Hausherr *et al.*, 2006). Detection of all empty regions, including voids, pores, delamination and translaminar cracks, can efficiently provide level of material porosity, as well.

Conclusions

NDT methods are very important for the analysis of CMCs in both operation and production. CMCs are a rather newly developed material class and their damage mechanisms have yet to be fully explained. Comprehensive analysis is still needed to ensure the production of defect-free components. The high costs of CMCs and their highly responsible applications require careful diagnostics, not only to ensure the quality of materials, but also for analysis of the production process and its optimization.

Each of NDT methods has advantages and disadvantages. Selection of the appropriate method requires a careful assessment of the requirements. The most commonly used method for detecting defects in CMCs is the Ultrasound method. It can be used to detect large pores and stratified surfaces. These methods can detect the depth at which the defect is located, but not its shape, which is why it is necessary to test in several perpendicular planes or combine the test with another method (e.g., radiographic method). Thermographic methods are suitable for mobile use, but have limited defect detection capabilities. Penetrant methods are simple and inexpensive but the disadvantage is that only surface defects can be detected. Radiographic methods are inexpensive and fast and can detect most of the defects that commonly occur in the CMCs. Radiographic methods can be applied in serial production, due to their fast analysis and low cost. The disadvantage of this method is that one image can be used to determine the shape of the defect, but not the depth at which it is located. Serious drawback of radiographic methods is safety measures that must be provided.

Computed tomography (CT) method is the most sophisticated non-destructive method available (Hausherr *et al.*, 2009). The ability of 3D analysis of complex parts without any sample preparation and very accurate data makes this method very effective. However, the method is currently technically limited to parts of relatively small dimensions (up to 50 cm). Cost of CT devices is still very high, thus limiting its application.

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Radiation Induced Effects in CMCs for Advanced Nuclear Energy Systems

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Introduction

Ceramic matrix composites are considered the highly promising candidate materials for use in the advance nuclear energy production systems and deep space propulsion systems. The extreme conditions that exist in such applications may result in major changes of material properties and significant limitation of the operational lifetime. CMCs have the potential to withstand these severe environments due to their overall physical and chemical stability, including excellent mechanical strength at high temperature, radiation resistance, relatively low neutron activation and chemical inertness. These characteristics of CMCs are advantageous for improving safety, reliability and accident tolerance of the fission nuclear reactors, both for those which are currently operating, and for the advanced Generation IV reactors which are in a design stage.

The safety requirements have been strengthened after Fukushima Daiichi accident not only for the fission reactors' normal operation and anticipated operational occurrences, but also for the containment performance of the reactor core and fuel structures in the case of both the design basis (DBAs) and beyond design basis accidents (BDBAs). The proposed Generation IV reactors (Kelly, 2014) will accommodate even higher operating temperatures and radiation fluxes than existing reactor types, and will utilize diverse coolants, which is very demanding from the chemical compatibility perspective.

Therefore, novel structural materials for the reactor core and nuclear fuel are expected to endure significant fluxes of high energy radiation, very high temperatures and corrosive environments over the extended reactor service life, and to preserve integrity under DBA and BDBA conditions for a prolonged period compared to the materials presently in use.

Silicon carbide (SiC) continuous fiber-reinforced SiC matrix composites (hereafter SiC/SiC) have been investigated as a novel fuel cladding for light water reactors (LWRs) (Duan *et al.*, 2017) and as a structural material for a fuel assembly duct (channel box) in boiling water reactors (BWRs). SiC/SiC can maintain high strength to temperatures above 1400°C (Shimoda *et al.*, 2011), perform much better than a zirconium (Zr) based alloys under steam or water at high temperature (Hallstadius *et al.*, 2012), have exceptional oxidation resistance (Braun *et al.*, 2017) and lower hydrogen production in anticipated operational occurrences (Duan *et al.*, 2017). Due to these characteristics that are superior to Zr-based (Cr-coated) or FeCrAl cladding materials, nuclear-grade SiC/SiC is assumed as the supreme cladding material in the development of the accident tolerant fuel (ATF) concept. Furthermore, the SiC fibers provide extra support for enduring localized fractures, so the ATF cladding would not fail catastrophically in DBAs and fission products would be confined. Additionally, SiC has even lower neutron capture cross section than Zr (George *et al.*, 2015), which is beneficial for the neutron economy in LWRs (Younker *et al.*, 2016).

The innovative fuel types such as the fully ceramic microencapsulated (FCM) fuels have been proposed for use in the current and advanced LWRs (Terrani *et al.*, 2012), and in high temperature gas cooled reactors (HTGRs) (Lu *et al.*, 2018) FCM fuels are based on the well established microencapsulated fuel technology such as the tristructural isotropic (TRISO) fuel that has achieved a superb performance record in conventional high temperature gas cooled reactors (HTGRs) (IAEA, 2010) over several decades. A TRISO fuel particle consists of a nuclear fuel kernel enveloped by 3 concentric spherical layers: the buffer (porous carbon), inner pyrolytic carbon (iPyC), SiC and outer PyC (oPyC) (Powers *et al.*, 2010). Each layer serves a particular purpose and contributes to thermo-mechanical strength and the containment of fission products, enabling both high temperature and burnup margins. In FCM fuels there is an additional barrier to prevent fission product release since TRISO fuel particles are implanted in a dense SiC matrix (Terrani *et al.*, 2012). Microencapsulated fuel technology has also been considered for use in Generation IV Molten Salt reactors (MSRs), in particular fluoride salt (FLiBe) cooled high-temperature reactor (Qualls, 2017). Furthermore, the excellent engineered barrier shell of TRISO fuel has been recognized as a potential solution for nuclear waste disposal in a geologic repository, in proposed deep-burn fuel cycle (Rodriguez *et al.*, 2003). Generally, inert ceramic matrices have been proposed for the nuclear and other radioactive waste management solutions (Ewing and Lutze, 1991; Matovic *et al.*, 2013), and SiC matrix has been proposed for the immobilization of isotopes ^{14}C , ^{129}I & ^{85}Kr from the spent nuclear fuel reprocessing (Strachan *et al.*, 2009).

In fusion energy systems SiC/SiC composites are considered for structural and functional applications for the in-vessel components of magnetic confinement fusion systems. This includes blanket structures, plasma-facing components (PFCs) (Nygren *et al.*, 2016), and flow channel inserts (FCIs) in the dual coolant lithium lead blanket (DCLL) concept (Smolentsev *et al.*, 2015). FCI is the lining of the LiPb channel that separate high temperature LiPb flow from the reduced activation ferritic/martensitic steel (RAFM) structure and isolates LiPb thermally and electrically.

CMCs capable to fulfill demands of the outlined nuclear energy systems, primarily stability under irradiation, are denoted as "nuclear-grade". Nuclear-grade SiC/SiC is manufactured from stoichiometric, high crystalline matrix with a minimum of secondary phases, infiltrated in near stoichiometric Generation III SiC fibers. Chemical vapor infiltration (CVI) process is preferential for obtaining higher purity at low infiltration temperature and pressures, and lower residual stresses (Kondo *et al.*, 2011; Naslain, 2004; Katoh *et al.*, 2014). Nano-infiltration transient eutectic phase (NITE) process is also used to fabricate SiC/SiC with nearly fully dense matrices and higher thermal conductivity, that is required for certain applications (Koyanagi *et al.*, 2014).

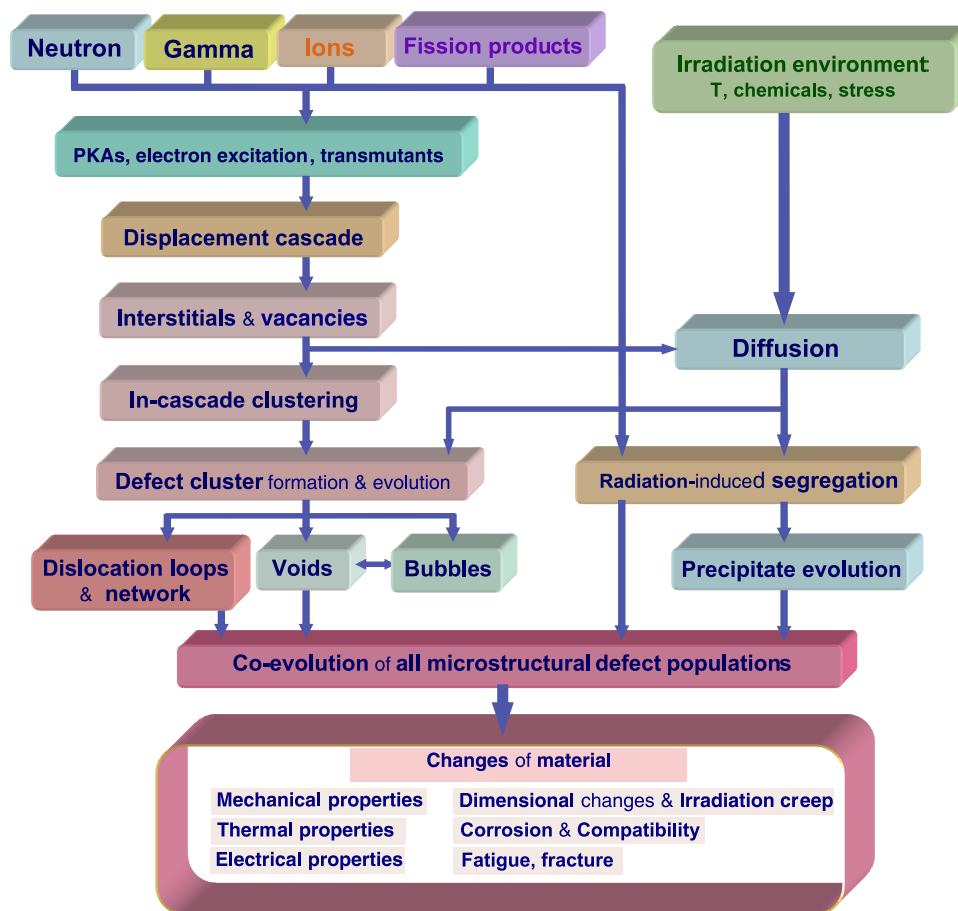


Fig. 1 Flow diagram of radiation induced processes and damage evolution in material. Adapted from Azevedo, C.R.F., 2011. Selection of fuel cladding material for nuclear fission reactors. *Engineering Failure Analysis* 18, 1943–1962 with permission.

Carbon-fiber-reinforced carbon (C/C) composites are also considered for use in fission HTGRs and fusion reactors (Tivey *et al.*, 2001), and since C/C have been extensively used in advanced applications, their technology and fabrication are well established. The strength of C/C is greater than that of nuclear graphite, and its activation by neutrons is low. The C/C have favorable inherent thermal properties, such as extremely low thermal expansion, thermal shock resistance and enhanced thermal conductivity (Oku, 2003) which can be improved to meet specific requirements by tailoring fiber architecture. The main advantage of C/C for use in a fusion reactor is their very high thermal conductivity, which can dissipate the intense thermal flux generated by the plasma (Missirlian *et al.*, 2011). However, the exploitation of C/C is limited to low dose applications due to their dimensional instability under neutron irradiation and onset of structural disintegration (Burchell, 1996). Also, a dramatic drop of the thermal conductivity was reported even at very low fluences and irradiation temperature of 200°C (Maruyama and Harayama, 1992, Burchell, 1996). Additional limitation for the C/C use is that only environments without or with very low oxygen content are endurable.

The main difference of the fission and fusion energy systems' environment from other types of harsh environments is the presence of the intensive mixed radiation field, which induces additional degradation phenomena – radiation damage. The intention of this article is to briefly outline basic mechanisms and phases of CMC material modifications under ionizing radiation, from nuclear reactions with atoms of the composite material, production of primary knock-out atoms and transmutants, their further impact at the atomic level, throughout changes induced on microstructure and further progression to observable macroscopic effects on physical, mechanical, thermal and electrical properties of material. The focus is on the effects created by neutron and ion irradiation as the most significant for the considered applications, and the damage this ionizing radiation produces in silicon carbide materials which are the candidates for use in advanced energy systems. Schematic diagram of these various effects and processes which radiation induces in material, in synergy with other environmental parameters, is illustrated in Fig. 1.

Interaction of Radiation With CMC Material

In the advanced nuclear energy systems CMCs will be simultaneously exposed to high fluxes of various types of ionizing radiation, such as neutrons, gamma and beta rays, and charged particles (ions). Additionally, non-ionizing radiation is present in fusion

environment and in various space applications, where magnetic fields and electromagnetic forces exist as well. The primary sources of radiation in fission and fusion reactors are neutrons, having different energy spectra. The neutron spectra from ^{235}U fission is well-described by a Maxwellian distribution with a nuclear temperature of about 1.5 MeV, but the actual neutron spectrum in a reactor core varies depending on the reactor type. In thermal reactors neutrons are slowed-down due to scattering on light nuclides of a moderator (thermal neutron spectra), while in fast reactors, without moderation, neutron spectra are similar to the initial fission spectrum. The fusion D-T (deuterium-tritium) reaction produce a continuous flux of 14 MeV neutrons, which is modified by neutron interactions primary with the materials present in a first wall/blanket, although neutron energy distribution remains in the MeV range predominantly.

The neutrons interact with atoms of reactor materials even at very low energies, undergoing various nuclear reactions which result in production of atomic displacement cascades, transmutation of atoms and/or activation of irradiated materials. Elastic scattering of a neutron transfer a significant energy so that recoil atoms can be displaced from their equilibrium positions within a lattice, while inelastic (n, n') scattering can excite recoiling nucleus to a specific levels that de-excite by photon or charged particle emission, which, as a result, give an additional bang to the recoils. Nonelastic nuclear reactions of (n, x) type, where neutron is captured followed by the emission of one or more light particles, cause transmutation into a different isotope/element, which can be radioactive. The recoils resulting from the (n, x) reactions (i.e., the residuals in non-elastic nuclear reactions) also transfer energy to the lattice atoms. In addition, secondary radiation field from the decay of newly formed radioactive isotopes will increase the overall radiation level materials are exposed to. All these reactions and decay modes that may occur in the irradiated material induce various modifications and defects.

The primary (initial) recoil events following a nuclear reaction are referred to as the primary knock-on atoms (PKAs) or primary recoils. They further transfer kinetic energy to their surrounding atoms, displacing some of them from the lattice and causing damage in a material. The physical parameter that describes this radiation induced damage is defined as the threshold displacement energy (E_d) (Norgett *et al.*, 1975), which is the minimum amount of kinetic energy, transferred to a lattice atom that results in the formation of a stable Frenkel pair. E_d is dependent on orientation, so for ceramics, which generally consist of multiple sublattices, E_d has to be separately measured for each sublattice and also for different crystallographic orientations (Zinkle and Kinoshita, 1997). The number of atomic displacements produced by a primary recoil with an initial energy E can be roughly estimated by applying the Norgett, Robinson and Torrens (NRT) theory/method (Norgett *et al.*, 1975). The extent of the displacement damage is expressed by displacements per atom (dpa) - the international standardized parameter (ASTM E 521-96, 2000) which is used to obtain an estimate of the number of atomic displacements that could be generated by the energy radiation has deposited into a material.

The PKA energy distribution is different for each type of reaction and depend on the incident neutron energy, the angle between the incident neutron and the final recoil directions, as well as the masses involved (Greenwood, 1994). The PKA energy spectra might be modified because of the material composition changes under transmutation. Also, transmutation products that are radioactive can create additional PKAs through their subsequent decay. The contribution of these PKAs to the total PKA population might not be insignificant as the irradiation time increases, and the analysis of (Gilbert and Sublet, 2016) demonstrates that this is particularly manifested for light materials. More importantly, after irradiation is shutdown, the “decay-PKAs” will be the only PKAs in the material, and therefore the only potential cause of damage accumulation. This implies that decay PKAs induce the damage in lighter materials which may be more significant.

In pure silicon PKA distribution the dominant PKA type across most PKA energies is Si itself, with a maximum PKA energy $E_{\text{PKA}} \sim 1$ MeV. Recoils from the elastic and inelastic scattering on ^{28}Si (the 92.23% naturally occurring isotope) give the main

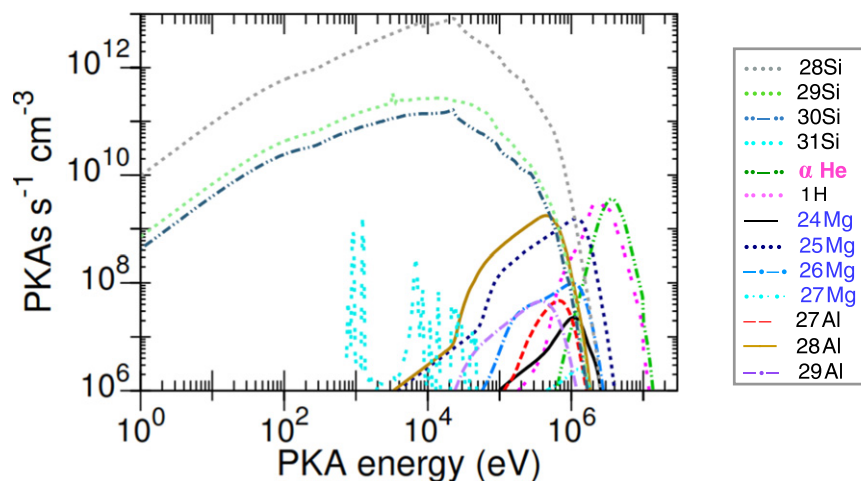


Fig. 2 PKA distributions for isotopes produced in pure Si irradiated by neutrons under conditions in fast breeder reactor (FBR) (from Gilbert, M.R., Sublet, J.-C., 2015b. UKAEA-R (15) 33 - supplement: PKA Distributions of the Elements Simulated Using TENDL-2014, FBR Nuclear Fission plants. UK Atomic Energy Authority with permission).

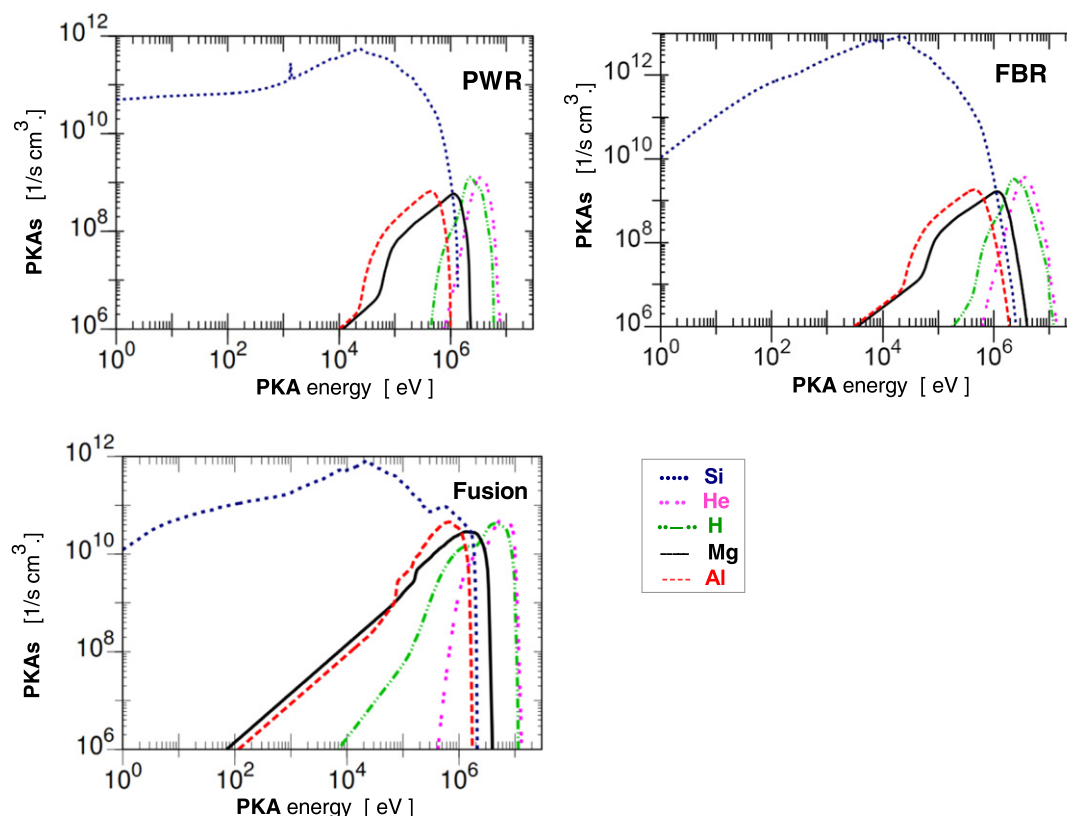


Fig. 3 Elemental PKA distributions for pure silicon Si irradiated under conditions in fission reactors: (a) PWR, (b) FBR and (c) DEMO FW reactor (from Gilbert, M.R., Sublet, J.-C., 2015a. UKAEA-R (15) 31 - supplement: PKA Distributions of the Elements Simulated Using TENDL-2014, PWR Nuclear Fission plants. UK Atomic Energy Authority. Gilbert, M.R., Sublet, J.-C., 2015b. UKAEA-R (15) 33 - supplement: PKA Distributions of the Elements Simulated Using TENDL-2014, FBR Nuclear Fission plants. UK Atomic Energy Authority. Gilbert, M.R., Sublet, J.-C., 2016. CCFE-R(16)36 - supplement: PKA Distributions of the Elements Simulated Using TENDL-2015, Magnetic Fusion Plants. UK Atomic Energy Authority, with permission).

contribution, while other two natural isotopes, ^{29}Si and ^{30}Si , contribute to total silicon PKA evenly, as shown in Fig. 2. Additional heavy recoils' PKA-types come from magnesium (Mg) and aluminum (Al) that are also produced. Secondary emitted light gas particles of hydrogen (H) and helium (He) are further PKA distributions, which are mostly dominated by ^1H and ^4He from (n, p) and (n, α) reactions, respectively (Gilbert and Sublet, 2015b).

The interactions of neutrons with reactor materials depend strongly on the incident energy spectra. Elastic and inelastic scattering are dominant reaction channels for neutron energies below 1 MeV, while above a few MeV many more reactions become relevant, consequently producing a more complex distribution of PKAs in both energy and type. Also, the cross sections for reactions that lead to transmutation increase rapidly above a few MeV. Scattering of the 14.1 MeV neutrons from the D-T fusion produce primary knock-on atoms with higher energies than PKAs occurring from a fission spectrum, which results in additional lattice displacements (Stork and Zinkle, 2017). Consequently, radiation damage for a D-T fusion reactor materials is expected to be considerably augmented compared to damage in fission reactors.

The PKA distributions in pure silicon that are produced by different neutron spectra which are typical for the pressurized water (PWR) and fast breeder (FBR) type fission reactors, and for the fusion DEMO reactor, are shown in Fig. 3. These PKA spectra are calculated by FISPACT-II and SPECTRA-PKA codes using TENDL-2014 nuclear data library (Gilbert and Sublet, 2015a,b, 2016).

Atomic Displacement Damage and Transmutation in CMC

The exact PKA energy distribution has to take into account contributions from all nuclear reaction channels in order to evaluate the initial damage formation accurately. The primary and higher order recoils produce a displacement cascade through an iterative process. Specification of the PKA types, their energy spectra and spatial distributions are necessary as an input to computational simulation that predict the formation, evolution and behavior of radiation induced damage.

Various analysis of atomic displacement damage in different fusion and fission spectra have shown that around 95% of the total damage is produced by neutrons with $E > 0.1$ MeV (Heinisch et al., 2004), which have the relatively high dpa cross section (Fig. 4). Moreover, the radiation damage parameters in a fusion environment depend on the employed confinement system (an inertial (IFE) or a magnetic (MFE)) due to significant geometrical and spectral differences between those systems, and also on

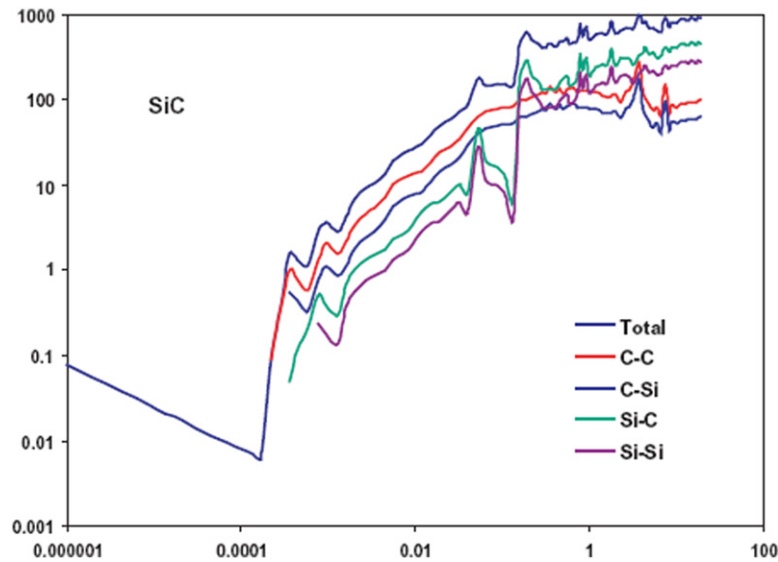


Fig. 4 Total dpa cross section for SiC and individual contributions from each PKA-target atom (from Heinisch, H.L., *et al.*, 2004. Displacement damage in SiC irradiated in fission reactors. *Journal of Nuclear Materials* 327 (2–3), 175–181, with permission).

materials used in the blanket design. For the same fast neutron fluence ($E > 0.1$ MeV) displacement damage at the first wall (FW) of fusion system is elevated compared to damage in significantly softer fission spectra where fractions of low energy neutrons are higher and peak energies are lower. The fraction of the neutrons with energies > 0.1 MeV is only 25% in the spectrum of High Flux Isotope Reactor (HFIR) at ORNL (Binford and Cramer, 1964), while it is $\sim 75\%$ at the first wall of a blanket in fusion system. Damage is similar in different fusion systems, i.e., almost the same in D-T and D-D (deuterium- deuterium) spectra (Guo *et al.*, 2014) while dpa values obtained by (Sawan, 2012) for the IFE confinement system are slightly lower than in the MFE system for the same neutron wall loading of 6 MW/m^2 .

The amount and the elemental mix of gaseous and metallic transmutants produced in SiC also depend on the neutron spectrum. The cross sections for reactions that lead to transmutation increase rapidly above a few MeV and usually have threshold energy (1–10 MeV). For the same fast neutron fluence ($E > 0.1$ MeV), yield of the metallic transmutation in fission reactors is about an order of magnitude lower compared to fusion systems (Sawan *et al.*, 2013). Also, due to the harder spectrum in MFE transmutations produced in SiC are a factor of 2 higher than in IFE system. The dominant transmutation product in softer fission spectrum ($\sim 76\%$) is phosphorus (P) from (n, γ) reactions on Si followed by β decay. Phosphorus contributes with only 3% to impurity production in fusion systems. Reactions of high E neutrons with carbon (C) create beryllium (Be), lithium (Li) and boron (B), while interactions with Si produce Mg and Al. Production of these elements is higher in fusion systems due to harder neutron spectrum than in fission reactors. Mg is the most abundant metallic transmutant in fusion systems with more than 50% contribution, while it is present with only 16% in fission reactors (Sawan *et al.*, 2013).

Generation of gaseous transmutation products He and H in SiC becomes considerable for the neutron energies above 5 MeV, since He and H are created by nuclear reactions such as (n, α) , $(n, n\alpha)$, (n, p) , (n, np) (ENDF/B-VII.0). The fission spectra in HTGR and HFIR reactors produce an amount of He and H that is one order of magnitude lower than that of the fusion DT and DD spectra (Guo *et al.*, 2014) due to the smaller fraction of neutrons with $E > 5$ MeV.

Neutron Induced Activation of CMC

The secondary radiation from the neutron induced activation in material might be present post-irradiation for various time periods, and therefore has to be considered during scheduled maintenance of a nuclear facility, and for disposal of components and materials. This is particularly important for fusion reactors' operation, where contact dose rate of a component/material determines whether that component could be handled hands-on or remotely, with maximum dose rate limits being $10 \mu\text{Sv/h}$ and 10 mSv/h , respectfully (Forty and Cook, 1997). In the case that long lived nuclides are present, the disposal of material must be performed in a way that conforms to the relevant safety requirements of the radioactive waste management (IAEA, 2009).

Pure SiC has superior short-term activation properties compared to other low-activation materials currently considered for advanced energy systems. These properties remain when impurities are added, if the amounts are controlled carefully (Forrest, 2000).

The long term activity of SiC is controlled by ^{26}Al with half-life $T_{1/2} = 7.2 \times 10^5$ years, and it is higher compared to other low-activation material such as reduced-activation ferritic/martensitic (RAFM) steels and vanadium alloys. ^{26}Al is produced by the following 2 step reactions: mainly by $^{28}\text{Si} (n, np) ^{27}\text{Al} (n, 2n) ^{26}\text{Al}$ and also by $^{28}\text{Si} (n, d) ^{27}\text{Al} (n, 2n) ^{26}\text{Al}$, (ENDF/B-VII.0;

Noda *et al.*, 2002). Since these reactions have thresholds near 13 MeV they are relevant for fusion reactor considerations. The radioactive ^{26}Al maintains γ activity for about 1 million years (Noda *et al.*, 2002).

Noda examined the influence of impurities on the induced activity of several SiC/SiC composites prepared in CVI process with Hi-Nicalon Type-S and Tyranno-SA fibers. Simulations were performed for SiC in the first wall of He gas and water cooled blankets which are neutron irradiated at wall loading of 10 MWy/m² in fusion reactor. Results revealed that among 35 impurities that were present, Al, zirconium (Zr), iron (Fe) and nickel (Ni) contributed to the dose rate of SiC/SiC composites mostly. Zr, Fe and Ni produce yttrium ^{91}Y ($T_{1/2} = 58.5$ day), manganese ^{54}Mn ($T_{1/2} = 312.5$ day) and cobalt ^{60}Co ($T_{1/2} = 5.27$ y), respectively, which keep the ~ 1 Sv/h dose rate for several tens of years (Noda *et al.*, 2002). The composite with Tyranno-SA fibers, containing the highest amount of aluminum (< 2%) has the activity levels of sodium ^{24}Na and ^{26}Al are higher than in other two composites examined, and 1% aluminium impurity produce the ^{26}Al activity which is one order of magnitude higher than those of other composites. Nevertheless, it was shown that dose rates of all examined composites would satisfy the assumed 10 mSv/h limit for remote handling after cooling for several tens of years.

Radiation Induced Defect Evolution in CMCs

There are many effects occurring throughout irradiation that changes material at the atomic and microscopic scale, consequently resulting in observable, macroscopic changes. Interactions of neutrons with material displace atoms from their lattice sites to the lattice interstices (self-interstitial atoms, SIAs) leaving the vacancies at their position, therefore creating a vacancy pair. A distribution of these point defects in the lattice is not homogeneous, and its dynamics depends on irradiation conditions, such as neutron fluence and temperature. A series of point defects produced by the primary knock-on atoms as it slows down result in forming a displacement cascade. Their creation and development are essential basis for the description of damage morphology and for understanding all irradiation effects in CMCs. Defects can migrate, undergo recombination or be absorbed at a defect sink (e.g., grain boundary or void), and surviving lattice defects are in the form of point defects or defect clusters. Furthermore, defects interact with each other and restructure due to diffusion which is thermally activated, resulting in various defect species such as voids, bubbles, dislocation loops and precipitates that can be correlated to the visible effects of irradiation.

Most of fundamental understanding on defect formation in SiC can be obtained from modeling and calculation. Molecular dynamic (MD) simulations of high energy displacement cascades in SiC shown that isolated Frenkel defects represent more than 80% of the surviving defects in 3 C- SiC (Gao *et al.*, 2002), where carbon Frenkel pairs are dominant (Devanathan *et al.*, 1998a). Significant populations of directly (cascade) produced antisites are found in surviving defect populations (Devanathan *et al.*, 1998b).

Frenkel pairs are stable due to the strong, primarily covalent nature of bonding in SiC (Matovic and Yano, 2013), even for very small vacancy–interstitial separations. Structural and energetic characterization of intrinsic point defects and Frenkel pairs in the framework of Density Functional Theory (DFT) and Generalized Gradient Approximation (GGA) calculations revealed that Frenkel pairs are more stable than isolated single defects, especially for Si interstitials. (Lucas and Pizzagalli, 2007). Fig. 5 illustrates two Frenkel pairs with different vacancy–interstitial separation in a Si vacancy and a Si interstitial configuration.

Probable recombination paths for various Frenkel pairs in the neutral state, including those formed by defects on different sublattices (i.e., C and Si), can lead to perfect sites and to antisites. Recombination barriers calculated in the framework of DFT were substantial for both C and Si Frenkel pairs (Roma and Crocombette, 2010). The recombination of close Frenkel pairs is essential for looking into details of the point defects and annealing mechanisms.

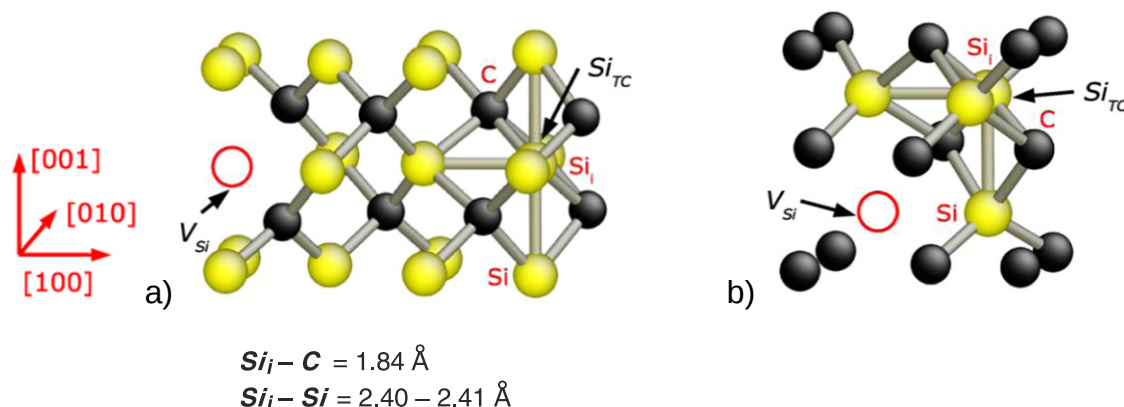


Fig. 5 Frenkel pairs relaxed configuration for a Si tetrahedral interstitial with a vacancy along: (a) [100] direction and (b) the [111] direction. Relevant interatomic distances are specified. Si and C atoms are represented as yellow and dark gray spheres, respectively. From Lucas, G., Pizzagalli, L., 2007. Structure and stability of irradiation-induced Frenkel pairs in 3C-SiC using 1st principles calculations. Nuclear Instruments and Methods in Physics Research B 255, 124–129, with permission.

Microstructural examination of high-purity, polycrystalline β (cubic) CVD-SiC irradiated by neutrons revealed various defect populations that are developed depending on temperature and a neutron flux level. For irradiation temperature above 300°C, small defect clusters appearing as dark spots, often called "black spot" defects, were observed (Katoh *et al.*, 2006) by transmission electron microscopy (TEM). These black spots were also reported for irradiation at temperatures between 625°C and 1000°C, and were identified as Frank dislocation loops of interstitial type lying on the [111] lattice plane (Price, 1973; Yano *et al.*, 1988). In this temperature range black spots are accompanied with defect clusters which have collapsed into small dislocation loops. With further temperature increase Frank faulted loops become dominant as observed at ~1100°C (Senor *et al.*, 2003; Kondo *et al.*, 2009), and at ~1400°C (Katoh *et al.*, 2006), while dislocation structure develops into dislocation networks at ~1400°C (Katoh *et al.*, 2006; Senor *et al.*, 2003).

The complexity and nature of defect microstructure advance when mobility of vacancies become sufficient and vacancy clusters can be created, and voids begin to occur. Voids are observed at very low density under Si ion irradiation of 10 dpa at 1000°C (Katoh *et al.*, 2006), while under neutron irradiation formation of voids is detected at 1250°C and neutron fluence of $\sim 4.3 \times 10^{25}$ n/m² (Price, 1973). The averaged size of defects increases and the number density decreases with elevating irradiation temperature, compared for the same neutron fluence (Katoh *et al.*, 2006; Price, 1973). A positive dependence of the defect size on the neutron fluence is also noticeable, so the Frank faulted loops grow to larger sizes when dose level at $T = 1400^\circ\text{C}$ increases from 10 to 30 dpa (Katoh *et al.*, 2006) and the size of the largest voids rise with increasing the fluence at 1250°C or 1500°C, as reported by Katoh and Price, respectively. At higher temperatures (e.g., 800°C–1300°C) the dominant defects observed by TEM become Frank faulted loops of interstitial type (Price, 1973; Senor *et al.*, 2003).

The described radiation-induced defects alter the microstructure of SiC and contribute to significant modifications in its physical, mechanical, thermal and electrical properties of the material. Long-term defect evolution is of particular importance because it directly impacts SiC material performance and the length of its service life in a nuclear application.

Radiation Effects in SiCf/SiC

Dimensional Changes

Swelling and amorphization

Dimensional expansion, or volumetric swelling, of SiC induced by irradiation in a condition without stress or constrain, is an important inherent property of SiC. Accumulation of strain due to defects in a SiC crystal irradiated by fast neutrons or self-ions can exceed a critical level at temperatures below $\sim 150^\circ\text{C}$ (i.e., critical amorphization temperature - T_{am}) (Newsome *et al.*, 2007) above which amorphization occur. Under self-ion irradiation at 50°C the swelling increases logarithmically as dose increases, proceeding saturation (Katoh *et al.*, 2006). For neutron irradiation at 70°C the swelling of amorphized SiC was determined to be 10.8% (Snead *et al.*, 2007). Above the critical T_{am} up to $\sim 900^\circ\text{C}$ the "point-defect" (or transient) swelling regime occurs, and exhibits saturation swelling at relatively low dose of a few dpa. Dimensional expansion and lattice spacing in SiC irradiated in the point defect swelling regime (150°C–1000°C) appeared to be in a fairly good agreement examined by X-ray diffractometry (Snead *et al.*, 2007). This regime is particularly relevant for nuclear fission applications (Zinkle and Was, 2013).

The level of saturation swelling decreases steadily with elevating irradiation temperature, until zero value is reached. This is credited to the temperature -dependent mobility of both Si and C interstitials which becomes considerable at temperatures approaching 1000°C, and causes that rather small portion of defects following cascade events survive. On the other hand, defect structure gains complexity above 1000°C since diffusion is enhanced, Frank faulted loops dominate and developing of voids commence slowly, resulting in the onset of property changes. For irradiation temperatures beyond $\sim 1000^\circ\text{C}$ up to $\sim 1400^\circ\text{C}$, there is a combination/ of the transition swelling that saturates and the slowly developing void swelling caused by escalation of vacancy clusters (Snead *et al.*, 2007). Above 1400°C voids become major contributors to swelling in the void swelling regime.

Magnitude of volumetric swelling of CVD SiC in transient regime for a few dpa dose level is $\sim 0.5\%$ at 600°C ion irradiation (Koyanagi *et al.*, 2013), while neutron irradiation causes $\sim 0.2\%$ swelling at 1100°C, reaching more than 1.5% at $\sim 1470^\circ\text{C}$ (Snead *et al.*, 2007). The trends of the NITE-SiC and CVD SiC swelling behaviors in the point-defect saturation regime agree well (Terrani *et al.*, 2018), as illustrated from various data sets in Fig. 6.

Under equivalent neutron irradiation conditions, up to 900°C, the nuclear grade CVI SiC/SiC composites with various fibers also exhibit swelling profile comparable to that of CVD SiC, although the composite swelling generally seems slightly less than the swelling of monolithic CVD SiC (Newsome *et al.*, 2007; Katoh *et al.*, 2014; Koyanagi and Katoh, 2017). No significant difference was found in the performance of the CVI SiC matrix, Hi-Nicalon™ Type S (HNS) (NGS Advanced Fibers Co., Ltd., Toyama, Japan) and the Tyranno-SA3 (TSA3) (Ube Industries, Ube, Japan) fibers. However, the differential swelling was observed between the NITE- SiC matrix and the TSA3 fibers irradiated to 3 dpa by Si ions at 500°C–900°C (Koyanagi *et al.*, 2013). The higher degree of swelling of the NITE- SiC matrix is mainly attributed to the sintering additive.

Additionally, the new semi-empirical model of SiC swelling and measurement accuracy improvements employed by Katoh revealed slightly anisotropic swelling behavior for the HNS SiC/SiC composite in the transition swelling regime and the temperature range of (260°C–280°C) under fast fluence of 1×10^{19} nm⁻². The deviation of the composite swelling behavior from that of monolithic CVD SiC is explained as the resultant of fiber architecture, the pre-existing microcracking, and specimen dimension. (Katoh *et al.*, 2018).

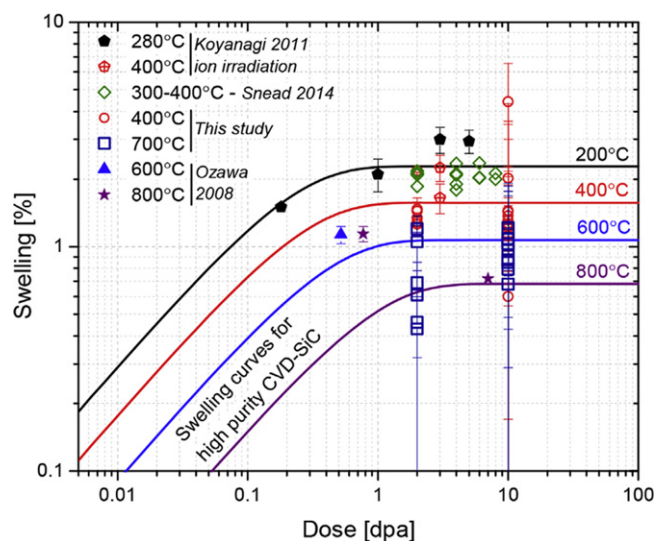


Fig. 6 Swelling of CVD- SiC and NITE- SiC as a function of dose and temperature. From Terrani, K.A., *et al.*, 2018. Irradiation stability and thermo-mechanical properties of NITE-SiC irradiated to 10 dpa. *Journal of Nuclear Materials* 499, 242–247, with permission.

Differential swelling and shrinkage

The differential swelling is the consequence of the diverse response to irradiation of the SiC/SiC components, i.e., SiC matrix, SiC fibers and the pyrocarbon (PyC) interphase, which can alter the original state of stress distribution introduced during the fabrication and accordingly degrade the composite's mechanical properties (Koyanagi *et al.*, 2013). Previously, SiC/SiC composites consisted of generations I and II SiC-based fibers (Bunsell and Berger, 2000), which densify when exposed to radiation and undergo significant volume shrinkage (Hollenberg *et al.*, 1995; Snead *et al.*, 2000b). A considerable disparity of dimensional change between the crystalline stoichiometric β -SiC matrix and the less crystalline, non-stoichiometric SiC fibers instigates a partial interfacial debonding at neutron irradiation dose as low as 1 dpa (Snead *et al.*, 2000b). Further dose level increase to 10 dpa causes complete interfacial debonding.

The current generation III of near-stoichiometric SiC fibers, such as TSA3 and HNS, do not exhibit substantial differential swelling (from CVI SiC matrices) since the radiation stability of fibers has been improved by decreasing the content of oxygen, free carbon and impurities, and increasing crystallinity (Ozawa *et al.*, 2007; Hegeman *et al.*, 2005; Snead *et al.*, 2000b). However, the fiber microstructure is still not the same as the microstructure of the CVI SiC matrices or monolith CVD SiC, and fibers still contain minor impurities such as oxygen (0.1–0.3 at%) in both TSA3 and HNS, as well as Al (0.2 at%) in TSA3 (Sauder and Lamon, 2007). It was demonstrated that boron, the sintering additive that replaced Al in the Sylramic™ (Dow Corning Corp.) fiber production, has an immense impact on strength and other mechanical properties of the composites irradiated by neutrons to doses ~ 2 dpa (Newsome *et al.*, 2007). Therefore, Sylramic™ fibers with the current features are not suitable for nuclear application.

Additionally, generation III SiC fibers contain free carbon as turbostratic C packets within the fiber, although less than previous fibers. Under Si ion irradiation of CVI-SiC matrix composites to 100 dpa at 300°C the volume swelling of the matrix was 2.5%, and the dimension stability of TSA3 fibers was observed (Kondo *et al.*, 2015). On the other hand, HNS fibers exhibited 0.8% axial and 0.7% radial shrinkage and notable reduction in the carbon packets population after irradiation to 100 dpa. The shrinkage of the fiber was primarily attributed to the significant increase in carbon antisites as underlying mechanism. The differences in the carbon packets distribution in TSA3 and HNS fibers before and after irradiation are illustrated in Fig. 7. The gap between HNS fibers and CVI-SiC matrix across the PyC layer increased after irradiation, as shown in (Fig. 8), where details of the gap difference between unirradiated and irradiation regions are given in magnified picture. Partial debonding at the fiber/matrix interface was also observed after n-irradiation of CVI-SiC matrix composites to 92 dpa at 319°C, accompanied with disappearance of the PyC contrast in SEM images (Koyanagi *et al.*, 2018).

The different responses to radiation of the composite's fiber, the matrix, and the interface may manifest as the reduction in crystallinity of the SiC phase, diminution of the grain size, reduction/redistribution in the free carbon packets population, material shrinkage and/or divergence in the magnitudes of swelling. The differential swelling modifies the residual stress in SiC/SiC composites and leads to interfacial debonding and occurrence of microcracks, which can occur at relatively low irradiation temperatures. The development of interphase damage and debonding in SiC/SiC composite under the Si ion irradiation to 5 dpa at room temperature is illustrated in Fig. 9 (Chai *et al.*, 2018). The microcracks and debonding are found to be the crucial reasons for the decline in the fiber/matrix interfacial shear strength (Katoh *et al.*, 2015; Chai *et al.*, 2018).

Combination of the components of SiC/SiC composites should be carefully designed to avoid significant degradation of properties, even though highly crystalline, stoichiometric β -SiC matrices and near-stoichiometric fibers of Generation III themselves lack the significant differential swelling or any other major changes in properties under irradiation at conditions previously

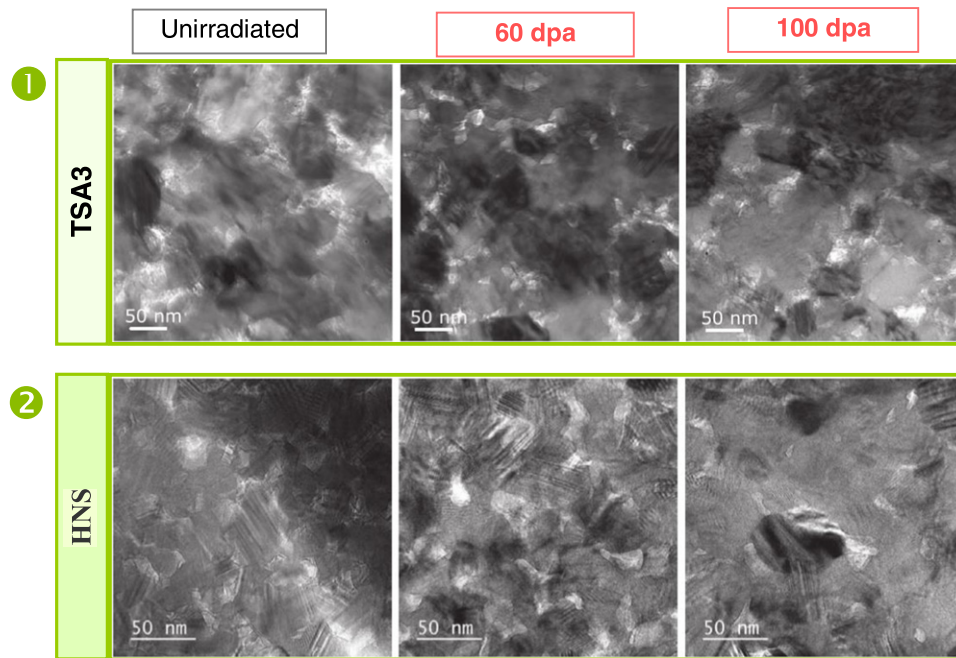


Fig. 7 The unirradiated and irradiated microstructures of TSA3 and HNS fibers. The magnification differs between each image in order to focus on the different size distribution of the carbon packets. From Kondo, S., *et al.*, 2015. Irradiation-induced shrinkage of highly crystalline SiC fibers. *Acta Materialia* 83, 1–9, with permission.

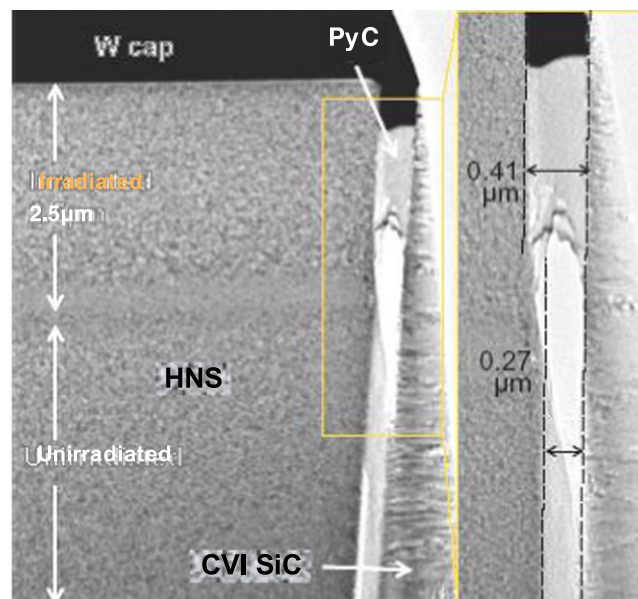


Fig. 8 Cross-sectional TEM image of the irradiated HNS SiC/SiC composite. The gap between the CVI SiC matrix and the HNS fibers increased after irradiation as shown in a magnified image in the yellow rectangle. From Kondo, S., *et al.*, 2015. Irradiation-induced shrinkage of highly crystalline SiC fibers. *Acta Materialia* 83, 1–9, with permission

discussed. In that regard, the major issues to be investigated about degradation of the SiC/SiC mechanical properties appears to be fiber/matrix interphase which loses its functionality under irradiation (Ozawa *et al.*, 2007). The PyC interphase response to irradiation is of particular interest and not adequately understood, despite widely-researched nuclear-grade graphite materials. It has to be clarified whether irradiated PyC interphase behaves similar to irradiated nuclear-grade graphite, considering crucial dimensional and mechanical differences between the unconstrained monolith material and the thin-layer interphase that is mechanically constrained on both sides by very high modulus SiC (Katoh *et al.*, 2014).

Mechanical Properties

The elastic modulus change of CVD SiC due to irradiation is consistent with the point defect swelling in the corresponding temperature range (150°C–1000°C), and approximately linear relationship is anticipated between the Young's modulus decrease and the linear swelling (Katoh *et al.*, 2014). Generally, reduction of modulus is greater at lower irradiation temperature and

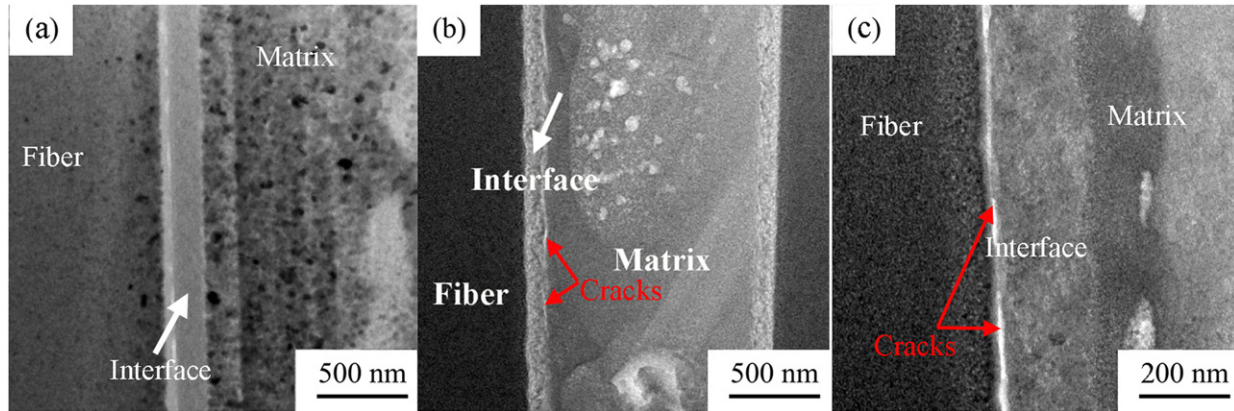


Fig. 9 TEM image of SiCf/SiC composites (a) unirradiated and Si ion irradiated at (b) 1 dpa, (c) 5 dpa (From Chai, Y., Zhang, H., Zhang, Y., 2018. Effects of Si ion irradiation on the interface properties of SiC/SiC composites. *Ceramics International* 44 (2), 2165–2169, with permission).

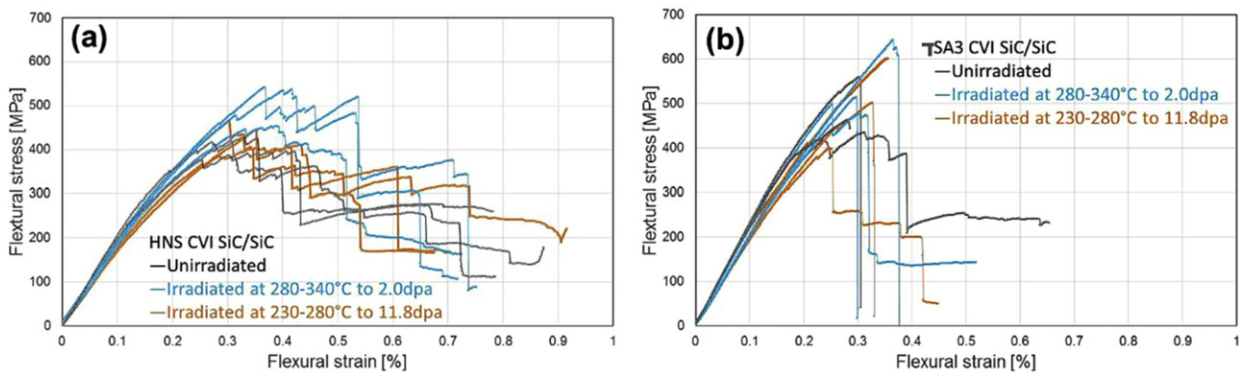


Fig. 10 Representative flexural behavior of unirradiated and neutron irradiated CVI SiC/SiC composites with (a) HNS and (b) TSA3 fibers. From Koyanagi, T., Katoh, Y., 2017. Mechanical properties of SiC composites n-irradiation irradiated under LWR relevant temperature and dose conditions. *Journal of Nuclear Materials* 494, 46–54, with permission.

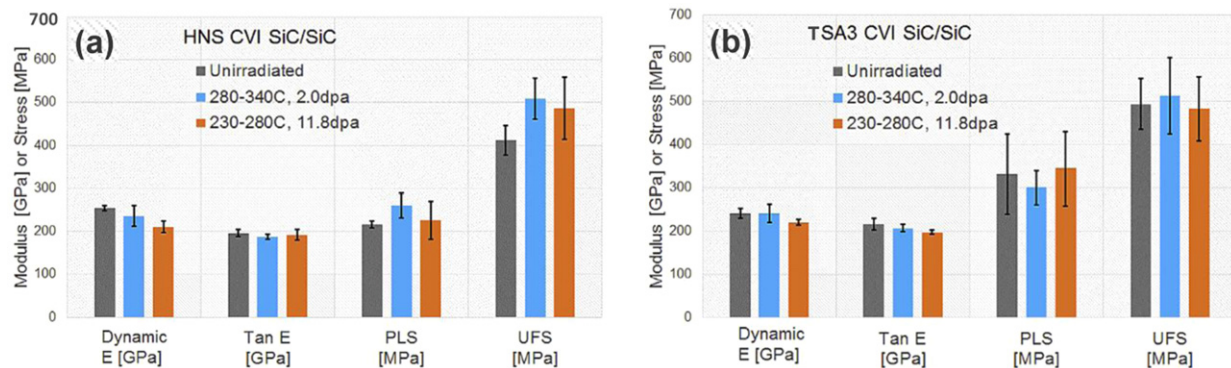


Fig. 11 The mechanical properties of unirradiated and neutron irradiated CVI SiC/SiC composites with (a) HNS and (b) TSA3 fibers: dynamic Young's modulus (Dyn E), tangent modulus of elasticity (Tan E), proportional limit stress (PLS) and ultimate flexural strength (UFS). From Koyanagi, T., Katoh, Y., 2017. Mechanical properties of SiC composites n-irradiation irradiated under LWR relevant temperature and dose conditions. *Journal of Nuclear Materials* 494, 46–54, with permission.

becomes negligible around 900°C and beyond. In the non-saturable swelling regime there is a little reduction in elastic modulus although the swelling is relatively large (Snead *et al.*, 2007). In spite of the decrease in elastic modulus, the general trend is that the irradiation-induced toughening of CVD SiC seems to be significant at 150°C–900°C, which confirms the increase in fracture energy by irradiation (Snead *et al.*, 2007).

For SiC/SiC composites reinforced with various SiC fibers the dynamic Young's modulus is also reduced by irradiation up to ~20% as reported by (Ozawa *et al.*, 2007; Koyanagi and Katoh, 2017). The dynamic Young's modulus was found to be higher than the tangent modulus of elasticity from the flexural tests performed by (Katoh *et al.*, 2015) and (Koyanagi and Katoh, 2017).

Strength properties of nuclear-grade SiC composites exhibit excellent radiation resistance at low to medium fluence levels (<12 dpa) in a broad temperature range and remain nearly unchanged as reported by (Snead *et al.*, 2000b; Newsome *et al.*, 2007) and (Katoh *et al.*, 2014). The CVI SiC composite with HNS fibers retained its flexural strength even after irradiation to higher neutron doses up to 40 dpa at 800°C (Katoh *et al.*, 2011). Representative stress-strain curves obtained by Koyanagi from the flexural testing of unirradiated and neutron irradiated CVI SiC/SiC composites with TSA3 and HNS fibers are shown in Fig. 10, while the results of the flexural behavior analysis are summarized in Fig. 11 (Koyanagi and Katoh, 2017). CVI SiC/SiC was

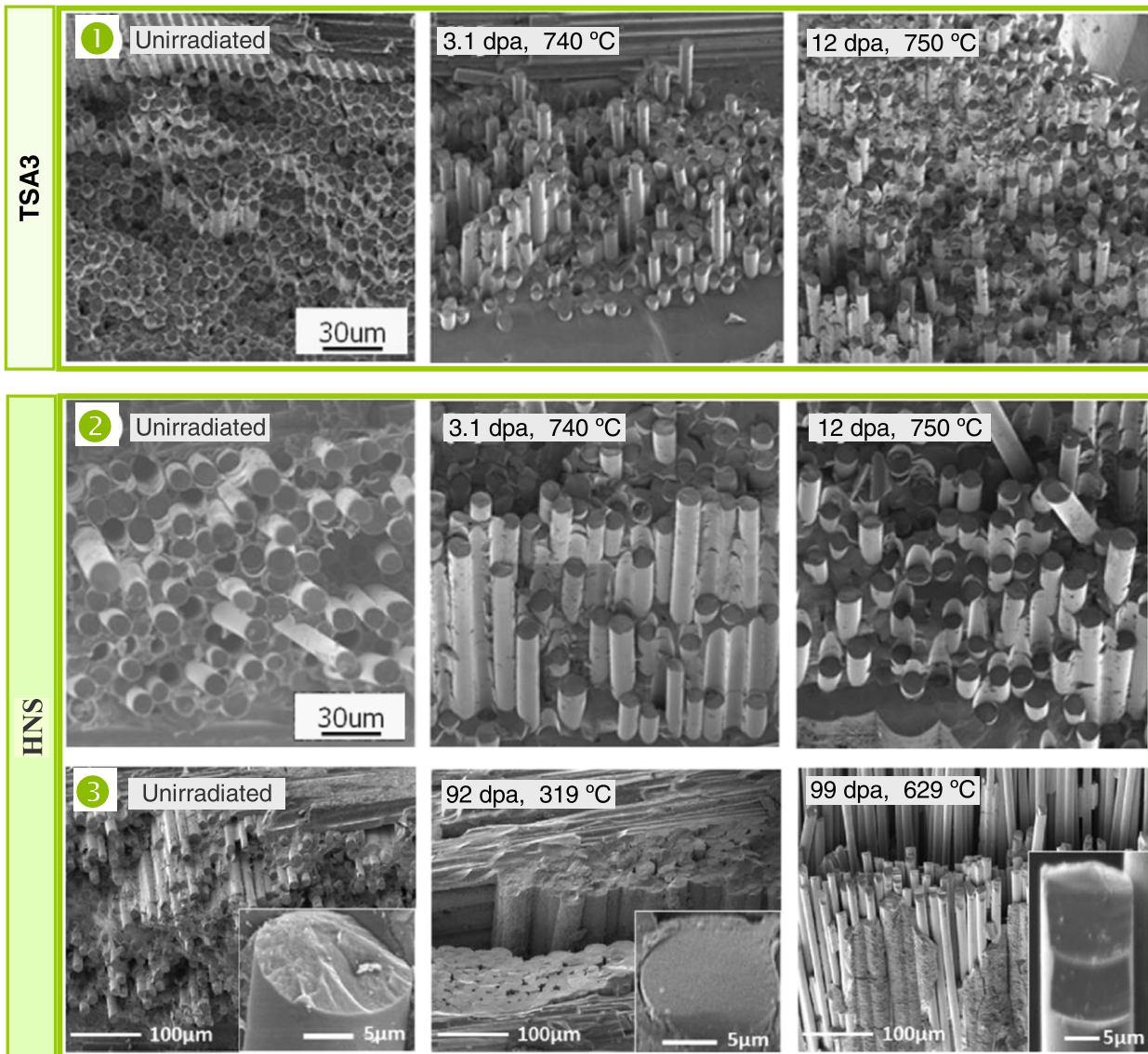


Fig. 12 SEM micrographs of fracture surfaces of unirradiated and neutron irradiated CVI SiC/ with: (1. row) TSA3 fibers, single-layer PyC interphase: unirradiated, irradiated to 3.1 dpa, 740°C and 12 dpa, 750°C. (2. row) HNS, single-layer PyC: unirradiated, irradiated to 3.1 dpa, 740°C and 12 dpa, 750°C (from Ozawa, K., *et al.*, 2007. Mechanical properties of advanced SiC/SiC composites after neutron irradiation. *Journal of Nuclear Materials* 367–370, 713–718, with permission). (3. row) HNS, multi-layer PyC: unirradiated, irradiated to 92 dpa, 319°C and 92 dpa, 629°C (from Koyanagi, T., *et al.*, 2018. Mechanical property degradation of high crystalline SiC fiber–reinforced SiC matrix composite neutron irradiated to ~100 dpa. *Journal of the European Ceramic Society* 38, 1087–1094, with permission).

irradiated to 2 dpa and 11.8 dpa at temperatures 230°C–340°C which are relevant for a LWR coolant. Nearly no change was found in the flexural strength (PLS or UFS) for the TSA3 CVI SiC/SiC composite, while some limited effects were found for the HNS composite. Both irradiated composites maintained their quasi-ductile fracture behavior exhibited before irradiation.

The absence of the mechanical property degradation observed under the considered range of irradiation conditions (dose < 12 dpa, $T < 800^\circ\text{C}$) was also confirmed by the microstructural stability of the composites. Typical fracture surfaces of composites' broken samples are illustrated for TSA3 and HNS composites with single-layer PyC interphase in the SEM images shown in rows (1) and (2) of Fig. 12, respectively. There were no notable changes of fiber pull-out before and after irradiation to 3–12 dpa, at $\sim 750^\circ\text{C}$ for both composites (Ozawa *et al.*, 2007; Katoh *et al.*, 2011). Fiber pull-out in HNS composites was longer than that in TSA3 composites regardless irradiation conditions. Fracture surfaces observed for the HNS fibers were rough before and after irradiation (Koyanagi and Katoh, 2017).

Higher radiation doses beyond ~ 40 dpa start to degrade flexural properties of composites at irradiation temperatures of $\sim 300^\circ\text{C}$ (Katoh *et al.*, 2015). The brittle failure of HNS SiC/SiC occurred after irradiation at 300°C to 92 dpa with significant degradation of both PLS and UFS, while at 629°C and 99 dpa nonlinear fracture behavior with apparent increased failure strain was exhibited (Koyanagi *et al.*, 2018). Microstructure of the fractured HNS SiC/SiC composite with multilayered PyC interphase was examined by SEM before and after irradiation, and images are shown in row 3 of Fig. 12. The relatively flat fracture surface with almost no fiber pullout observed for SiC/SiC irradiated at 319°C was consistent with its brittle flexural behavior, while fibrous failure was notable for sample irradiated at 629°C . The nonirradiated HNS fibers had rough fracture surface as expected, while irradiated fibers had relatively smooth surfaces.

The microstructural analysis also revealed that partial debonding at the fiber/matrix interface and disappearance of the PyC contrast occurred for dose of 92 dpa at 319°C , progressing to observable defects formed within the PyC layer at higher temperature of 629°C for 99 dpa (Koyanagi *et al.*, 2018). These alterations in the microstructure of the fiber/matrix interphase are found to be the cause of the observed strength degradation which confirmed previous conclusion of Katoh *et al.* (2015).

Thermal Conductivity

The thermal conductivity of the nuclear-grade composites resembles saturation behavior of the transient swelling, and saturates at relatively low fluence levels of a few dpa, depending on irradiation temperature (Snead, 2000a). There is no change in saturation behavior at higher fluences which is confirmed up to > 70 dpa at 800°C (Katoh *et al.*, 2014). The significant decrease in the thermal conductivity of SiC is due to the thermal resistivity of defects that occur in point defect saturation regime (150°C – 800°C) (Snead *et al.*, 2007). The defects that yield increase of thermal resistivity by scattering phonons also contribute to the macroscopic swelling (Terrani *et al.*, 2018). For high purity CVD-SiC the thermal resistivity is directly proportional to the macroscopic swelling in the material (Snead *et al.*, 2007).

Thermal conductivity of SiC/SiC differs depending on measurement direction, typically being lower in through thickness direction than in the in-plane direction (along one of the fiber axes). Thermal conductivity in both directions for SiC/SiC with various fibers and interfaces, neutron irradiated to ~ 6 dpa up to 1270°C is shown in Fig. 13 as a function of measurement temperature (Katoh *et al.*, 2014). This variation with orientation has to be carefully considered in applications for nuclear fuel

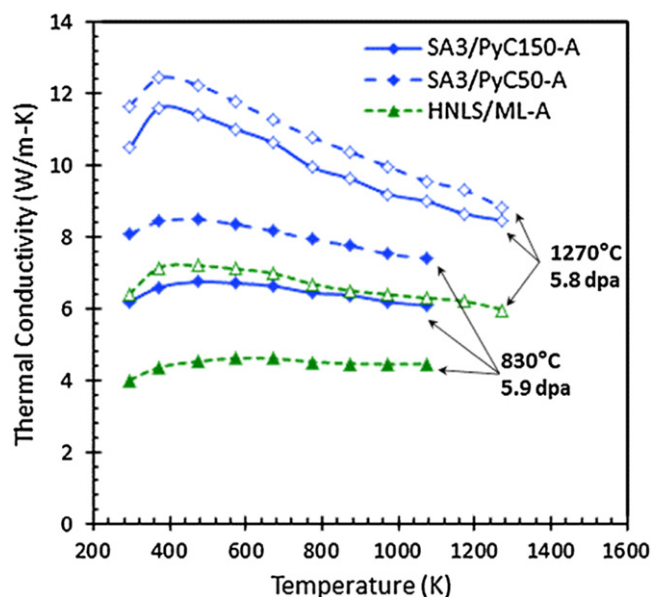


Fig. 13 Through-thickness thermal conductivity of neutron-irradiated 2D SiC/SiC with various fibers and interfaces. From Katoh, Y., *et al.*, 2014. Continuous SiC fiber, CVI SiC matrix composites for nuclear applications: Properties and irradiation effects. *Journal of Nuclear Materials* 448, 448–476, with permission

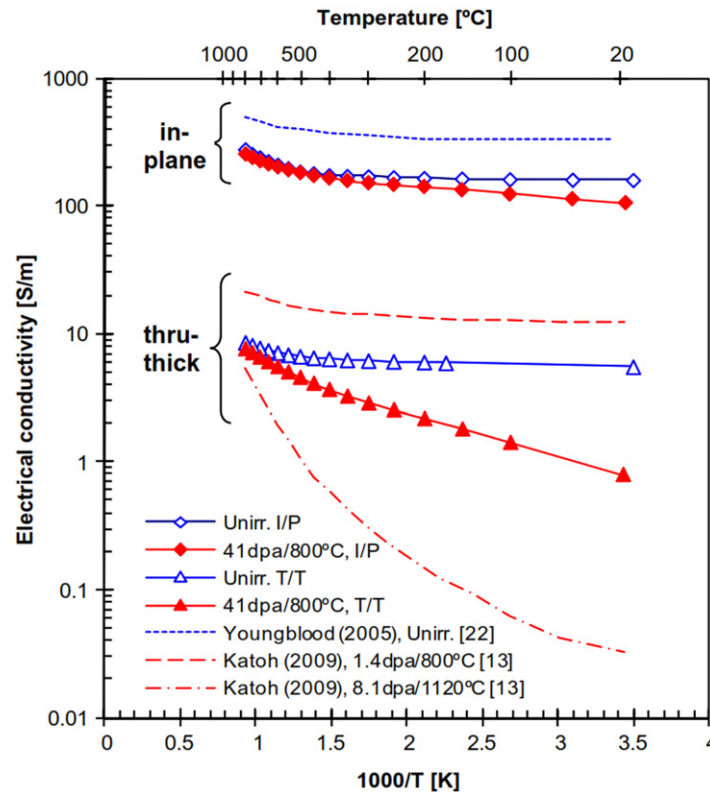


Fig. 14 Electrical conductivity of HNS CVI SiC matrix composites before and after irradiation up to ~ 40 dpa. From Katoh, Y., *et al.*, 2011. Stability of SiC and its composites at high neutron fluence. *Journal of Nuclear Materials* 417, 400–405, with permission.

cladding, which is exposed to significant heat flux from the fuel and under stress due to thermal gradients. For accomplishing stress mitigation and heat removal adequately high thermal conductivity is necessary. In order to provide for comprehensive modeling of cladding performance it has been suggested to measure thermal properties of SiC/SiC in multiple directions (Deck *et al.*, 2015).

Electrical Conductivity

Electrical conductivity of SiC/SiC composites is a principal characteristic for considering their applications in dual coolant lithium lead blanket (DCLL) concept for fusion systems. Flow channel inserts made of SiC/SiC line the LiPb channel to provide electrical insulation between the LiPb flow and the RAFM steel walls. Insulation is necessary to reduce the magneto-hydrodynamic pressure drop from the LiPb flowing alloy and prevent intolerably high stresses in the RAFM structure (Gonzalez *et al.*, 2016).

The electrical conductivity in the through-thickness and the in-plane (the direction of fibers) directions of CVI SiC matrix composite is generally determined by the significantly different conductivities of its components. The pyrocarbon interphase is much more conductive than SiC, nearly independent of temperature, and controls composite's conductivity below 500°C, when conduction through the SiC matrix starts to contribute (Katoh *et al.*, 2011). SiC is a wide-gap impurity semiconductor with a wide range of possible resistivities determined by the doping/impurity content and temperature, which can be tailored for a particular application (Stanković *et al.*, 2012). Under neutron irradiation the electrical conductivity of PyC may be changed by a factor of 2, depending on the irradiation condition and the initial quality of PyC (Katoh *et al.*, 2014), while its weakly dependence on temperature is maintained (Katoh *et al.*, 2011). The direct current electrical conductivities for both the in-plane and the through-thickness directions are plotted in Fig. 14 as a function of the measurement temperature. The electrical conductivities of composite irradiated to ~ 41 dpa at 800°C are found to be slightly lower than those before irradiation, in both directions (Katoh *et al.*, 2011). Generally, it can be considered that there is no substantial effect of irradiation on the electrical conductivity at high-temperatures.

Concluding Remarks

Ceramic matrix composites have potential for use as novel structural and functional materials in advanced energy production systems, and their behavior under irradiation, high temperatures and stresses have been widely researched over the past few decades. Manufacturing technologies advanced and the characteristics of SiC/SiC composites have been improved significantly. The current nuclear-grade composites with highly crystalline stoichiometric β -SiC matrices and Generation III, near-stoichiometric

beta-phase SiC fibers demonstrate certain stability under irradiation and do not exhibit substantial changes of property. Nevertheless, the specific features of composites' components such as the chemical impurities or additives, the inhomogeneity in grain microstructures or the presence of free carbon pockets, can impact the overall SiC/SiC behavior which need to be clarified. Additionally, understanding of the radiation response of the fiber/matrix PyC interphase is not adequate and has also to be improved. The irradiation stability of the fiber/matrix interface is found to be critically important for composite's performance under high-doses radiation in view of the fact that the interface loses its functionality due to radiation. Therefore, modification of the design of the fiber/matrix interface is a pathway for further improvement of radiation-resistance of SiC/SiC composite materials to enable their use in advanced nuclear systems.

The long-term composite behavior during operational life exposure in advanced nuclear facilities is of the particular interest. To assess material performance and damage evolution with a certain degree of confidence over such extended period require comprehensive understanding of underlying physical mechanisms. Radiation damage has multiscale character that covers wide ranges of time and dimension. The effects scale from atomic, point defect up to observable macroscopic level, with time periods spanning from 0.1 ps to decades of service lifetime. Various experimental and theoretical tools have to be utilized in an attempt to understand and describe fundamental processes of the formation and evolution of radiation induced damage, and to predict consequent behavior of the damaged ceramic material. Results of phenomenological and computational modeling and simulations have to be verified experimentally, in the representative high-dose radiation fields and other conditions relevant for the considered advanced energy systems. Operating fission research reactors and accelerator-based neutron sources can be employed for certain types of testing, but projected conditions in fusion facilities and most of the Generation IV fission reactors are beyond existing nuclear industry experience. One of the major challenges is the absence of experimental facilities which can provide the complex irradiation conditions resembling those in fusion systems.

Generally, material science is challenged to further improve fundamental understanding of radiation effects and damage evolution in SiC composites and their constituents, and to develop facilities for adequate material testing under aggressive conditions of advanced fission and fusion systems.

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Laser Physics and Modeling in Relation to Ceramic Matrix Composites

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Introduction

Composites have been in the focus of interest of various disciplines for a long time, starting from concrete in civil engineering. They have and had wide range of application- from mass media, to industry, traffic and many other areas of everyday life. In addition, when discussing the issue of composites, the following must be taken into consideration: sophisticated theoretic approaches, modeling of various composites, and prognosis of their technology, practical behavior, durability and different degrees of loading.

Due to the manifold advantages of their physical, chemical and other performances, composites have various applications in aviation, shipbuilding, medicine and even in the manufacturing of sporting and recreation garment and equipment materials (Zhang, 2015; Remond and Caron, 2020). The paper discusses selected problems in these dynamic areas. There are many connections and couplings from the aspect of laser techniques and composite materials in a very wide range of power and energy densities of quantum generators, various laser pulse-widths and variations of mono and multiple pulse expositions time.

For the purpose of diagnostics, laser damage is not assumed. However, LIBS (Laser Induced Breakdown Spectroscopy) and similar methods make very small local disturbances, and we do not consider such techniques when analyzing mechanical (and other) performances of composites under various stresses. Some methods, for example Brillouin spectra methods and methods of sound velocity evaluation/measurement, could be used for the evaluation of material dispersion. The values of sound velocity measured by mechanical methods, acoustic methods, as well as those with Brillouin spontaneous/stimulated scattering (Murayama *et al.*, 2004) reveal valuable information on optical anisotropy and various acoustical parameters. These and similar methods (such as elasto-optic effects and other techniques) present a way to detect stress both instantaneous and residual in a material.

Thermal performances of materials are measured using pulse methods for measuring thermal diffusion and similar data for different laser operation regimes (e.g., Nd³⁺:YAG, semiconductor lasers). The methods involve temperature measurement on both sides of the samples when laser beams of defined profiles propagate through the samples. Development of algorithms and data processing on final thermal performances of selected materials are still contemporary topics (Milošević, 2017). These techniques have been used in metrology for more than 30 years, but they are still improving and developing. Similar points of view and multidisciplinary approaches give direct or indirect answers for many new materials as well as for CMC. The porosity can be estimated through combining laser methods and ultrasonic ones.

CMC and composites in general are very specific materials of complex structures and require particular treatment. Depending on the composite type, they are often compared to the pure material such as metals, dielectrics, semiconductors, etc. The evaluation of an adequate theory and models (thermal, gaseous dynamical, similarity, basic, phenomenological, etc.) and of the algorithms developed should be given with defined approximations. It should be kept in mind that laser processing involves: cutting, caving, drilling, welding, soldering, surface treatment, micro-processing, rapid manufacturing, structuring, joining, plastic-metal connection, sintering, hardening and surface modeling (Olowinsky, 2019).

The experimental results of performed laser operations for selected composites are analyzed and presented using selected methods. The discussion will also cover other methods which might be of importance, but are not always included (thermal imaging during laser operation; detection, collection and processing of ejected material). It should be noted that there is a fundamental diversity between an analysis of the target material and ejected material, which could be further investigated. The thermal imaging application results should be the object of discussion depending on the laser working regimes i.e., pulse duration and repetition.

The thermal model derivation focuses on the thermal equation for chosen initial parameters, laser operation parameters, geometry of exposition, etc. Evaluation through laser numbers (Bass, 1983) can be chosen as a fast estimation of the efficiency of laser operation. If the pores are involved, a more sophisticated treatment through the Sierpinski carpet technique can be connected to ultrasound or opto-acousto-elastic methods, mentioned before.

Special attention should be paid to the laser damage, its definition and experimental methods for the damage performance assessment. Statistical treatment should be discussed and some insufficiently clear facts pointed out. Nanocomposites and their interactions with laser beams will be mentioned together with administrative regulations regarding the applications of laser technologies. These methods and elasto-optical and other methods present a way to decode/detect stress (instant or residual stresses/strains) in material.

Processes of New Composite Designing, and Generally Approach to Aging, Damage and Failures of Composite Materials

Theoretical and experimental assumptions should be provided in the form of modeling (either analytical or numerical) of aging, damage, failures. With regard to lasers, different degree of *interactions intensity* from modulation, damaging, up to disintegration or other possible relations in laser/composite interaction can be found.

Considering assumptions, unavoidable for modeling of the processes by computer support, methodical question could be: What analysis enable deeper presentation of the role – structural – simulations, modeling through computer support?

The development of the composite disintegration processes on micro- structural level related to components should be based on information such as fractography, micrographs, metallurgical investigations and methods based on diffraction structures, as well as other experimental methods.

In addition to the analysis of micromechanics of composite disintegration which demands investigation of real distribution of stress among components by deformation processes and abrasive damage registration, some new theories applied to recently developed materials are proposed (Fidanovski *et al.*, 2018).

This draws out a question of its relation to classic/modern theories under various applications' need (Aleksić *et al.*, 2015; Grujić *et al.*, 2010; Kaluđerović *et al.*, 2017; Srećković *et al.*, 2014). The increase of composite requirements is constantly emerging, and this is the reason why the most recent ones were mentioned. It immediately requires the new diagnostics of their behavior. One of latest theses at Belgrade University, related to composite with polyethylene terephthalate – PET and its recycling, was awarded as one of the best in 2019. New material composites are connected to various concrete composite armatures with added recycled poly/ethylene teraphthalate that has proved to be the good reinforcement in polymer composites. This involves fibers of modified and unmodified PET in complex structures. All mentioned are referring to the composites completely formed from the bio renewable sources.

Composite Materials Characterization With Contemporary Methods, Principal Performances and Defects

Processing of composites uses classic and modern methods. Principal operations in the processing are: cutting/sawing, grinding with carbide and diamond tools, water, laser or in wider sense other elion techniques. It means that laser, electron beam, neutron beams are included, but plasma can be added too, as well as, acoustical tools. Classical drilling (using mechanical borer, carbide tips, and grinding with diamond) are still topics of interest. Composite performances are better than that of homogeneous materials. One of the most important assumptions is that composites have very high coefficient of safety. In many new technologies applications composites have advantages, but in some cases they have disadvantages, too. Composite applications should be based on special analyses (theoretical estimation and practice).

Laser systems/stations could be utilized for drilling, cutting, engraving, glazing, and hardening. Particle (powder) production is also in the domain of laser material processing and as well as thin film production, cladding, coating or polishing, and transformation from anisotropic form to crystalline and vice versa. Composite control, nondestructive techniques NDT require specific development and modeling. The basic theories including physics/mechanics of fracture, estimation of material properties, mechanical, thermal, optical and other performances, now demand more complex and less conventional approaches. Each technological process/machining is characterized by special defects.

Composite/material defects are categorized with respect to the application selected, or manufacturing technology; details are presented in (Kutin *et al.*, 2007; Puharić *et al.*, 2007). The defects depend on the chosen technology and sequence of operation. Defects shapes depend on chosen operation: execution on material, in forming defined part of the construction, or methods of joining. This should be described (estimated, diagnosed and controlled), because integrity of finally obtained components, and systems, depend upon them. In Table 1, some defects on fiber material and their origin are presented. Note that in references (Kutin *et al.*, 2007; Puharić *et al.*, 2007) many very clear presentations of defects and explicit geometry of their design, but here we only anticipated some of them.

Monitoring systems (control) for composite materials include many standard and new methods (tensile, compression, bending measurement). Classical methods are: with tensile test devices, measuring devices based on resistivity change, etc. The destructive

Table 1 Frequent/common defects in composites

Number	Type	Origin/comment
1	Interlayer holes	Air plugs. Dislayering, deficiency of resine, etc.
2	Incomplete resin drying	Incorrect polymerization procedure
3	In excess matrix holes and porosity	Residual stress in materials irregular process execution/machining/; solidification composites in autoclave
4	Damaged fiber	Irregularity by maintaining and putting fibers in defined tool for polymerization. Fibers are sensitive to cross loading
5	Wrinkles, specific relief structures	Irregular setting and winding, in the case of glass and Kevlar fibers, they accommodate not so easily to tool contours with greater curves; inappropriate pressure at polymerization initiation
6	Inclusion of other material	Improper regulation and purity environment (Micro particles of dust), regulation of humidity and temperature of the environment where the operation involves settings of layers in the polymerization tool
7	Improper, unacceptable joining in layers	Irregular bonding of layers
	Thickness change	Insufficient/sufficiently resin leak during the polymerization process. Note that laser can be used in methods of polymerization

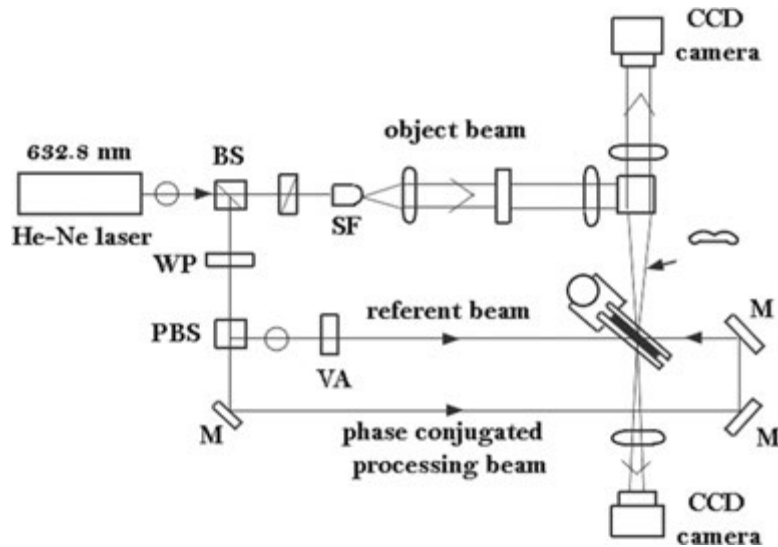


Fig. 1 The set up for holographic interferometry.

methods are: investigation of material loading to stretching-extension, compression, bending and wrapping (classic tensile machine, measuring resistance tapes, that have optical fibers as competitive method) (Uskokovic *et al.*, 1998; Krinulović and Srečković, 2001). Other methods are as follows: ultrasound, radiographic, neutrons flux based, X – and gamma rays, holographic, opto – elastics, Raman and Brillouin scattering.

The neutron radiography is applied for determination of debonding in sandwich structures. It has advantages and disadvantages. Disadvantage is blurring multiple defects in boundary areas of multilayer structures. Also, the neutron sources, demand special protection measures.

Holographic Interferometry

The principal role of holographic interferometry is in determination of debonding. The lighter zones in the micro records present areas that are not well adhered, linked to the processes of propagation, scattering, interference, diffraction of visible photons through materials. The porosity in adhering processes is presented by small circular areas or the defects. It is more difficult to determine a defect type, and carry out the diagnostics of humidity and corrosion processes. In the past these were the only possible methods for humidity determination. Today, the knowledge of measuring techniques is widened offering quality results and successful measuring rate. Methods of nuclear magnetic resonance are also at disposal. Mechanical cracks are of special interest.

Composites exist for a very long time as materials, e.g., concrete, and parchment, but the term “composite” attracted the full attention in research in relatively short time. The monitoring of composites can be organized in various ways. The first is to embed fibers composite and then stress can be measured by monitoring intensity of coherent light propagating through loaded fiber. In this way recognition of vehicles on the highways is achieved (Krinulović and Srečković, 2001; Barrias *et al.*, 2016). The first method can be also used not only on highways but in bridges and complex construction by observing the propagation of light and its changes in intensity, polarization, etc.

The other way is based on holographic techniques (cw and pulsed), use of laboratory equipment, with models imitating real structures made of transparent or materials with special reflectivity; holographic interferometry in various dispositions, **Fig. 1**. Relatively recently very fast/short laser pulses are used for at least picosecond spectrography/holography and they work in the laboratory as well as in the field.

X Radiography

Radiography with parameters 10–60 kV, 5 mA is in the class of low voltage radiography and it is applicable for composites. As previously mentioned, lighter or darker zones can be seen in micrographs taken in microscopic analyses. The light areas are related to the ranges with excess resin. Trench where resin was moving during polymerization is visible, too.

Considering nowadays nanocomposites, only one example is presented. Even that concrete is one of the oldest composites, it is still widely applicable in every days life. It is found that preparation of lightweight concrete exists with lingo cellulosic fibers from *Posidonia oceanica* balls (kuqo *et al.*, 2018). These fibers, possessing interesting properties resistance to fire and moisture, are found in large amounts along the Mediterranean shores and represent row materials for composite production at low cost. Flexural and compressive resistance of these fibers are defined recently and therefore have important role in production of lightweight concrete (Kuqo *et al.*, 2018).

Strain/deformation investigations are possible using new spectroscopic methods including Brillouin, Raman by line shape characteristics, the positions of maximums and minimums and changes (Vigolo *et al.*, 2009). For decoding of the obtained results,

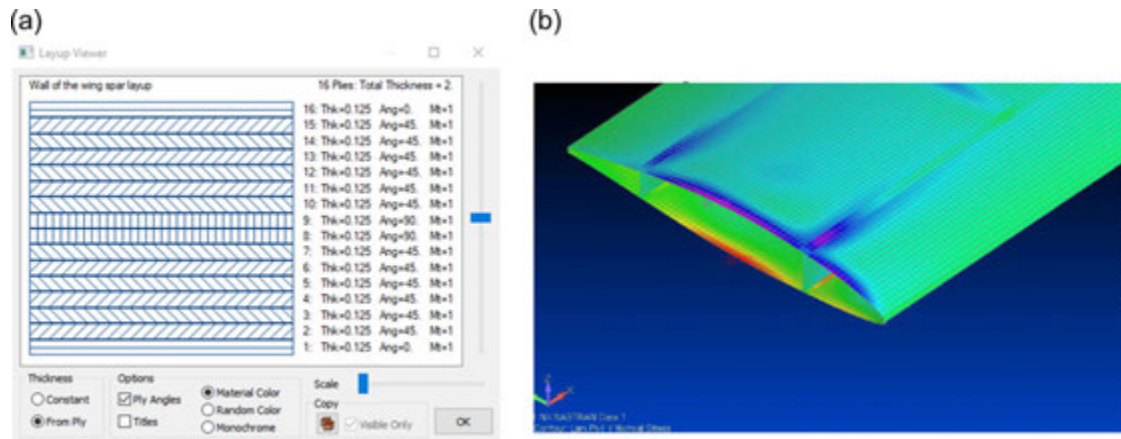


Fig. 2 (a) Wall of the wing spar layout and (b) normal stress in Y direction.

of Brillouin spontaneous/stimulated scattering, the specific numerical methods were developed. The changes of the dispositions between laser beams and polarized components in chosen geometry present very sophisticated links to elastic constants of the materials and the model applied. Besides, various components models can be tested by holographic methods in air tunnels testing, mentioned X radiography, and acoustical emission methods.

Composites in Aircraft Application

Composites still have the wide application in aircraft as well as sporting requisites industries (Fig. 2). The manufacturing of complex components and models for tunnel testing in the domain of high technology is based on contemporary methods and processes (Ristić *et al.*, 1993).

In order to reduce stresses (normal and shear) and to limit cracks under load, various analyses should be made. Composite/hybrid material is of particular interest in improving the performances through some changes in manufacturing and constructional technologies. Composites, especially reinforced with carbon fiber are light, strong and stiff. Aircrafts are thus lighter and more fuel efficient, benefiting the environment. Composite, construction, wing, tensile, normal, and shear stresses are the key words (Grigorova *et al.*, 2018; Dinulović, 2008; Kostić and Dinulović, 2020). Characterization of materials is shown in Fig. 2, where 3D CAD Software package is used, based on the FEM method. The wing and elements were as of AS4-3501/6Epoxy. Some data are: wingspan = 4860 mm, $m = 600$ kg, aeroprofile, coefficients of loading, program paquette Catia V5 as STP file, imported in Femap, created material is lamine, etc. At the end glass plastics, ceramics etc, were added in the aim of reinforcing construction/economics of mass/price. First are definitions of material in Femap using criteria Tsail Wu, TSail Hill, for different loading. The tasks are: producing laminates, their visualization for all parts of wing, distribution of normal stresses in x, y, z and shear stresses, as well as distribution of squeezing (Vigolo *et al.*, 2009).

Composites in Sporting Equipment

Many sports equipment and sport's world records are based and depend on composites. Some of them are with CMC, where the general aircraft are again on the top, representing the role of material through years and special designation (Fig. 4).

Special applications of CMC composites are in (Zhang, 2015; Remond and Caron, 2020; Halbig *et al.*, 2013) oxide/oxide CMC mixer nozzle assembly, including metallic attachment rings, mixer nozzle (AE3007). Explicit CMC is a base for center body, mixer nozzle, and 4 segments – CMC Outer shrouds.

Progress is constant in CMC component for aircraft. Example is a CMC combustor and its advantages and disadvantages (w/EBC). Various material and behavior after various cycles of operation, Table 2 could be one example.

Tennis racquets, ski equipment (skis and ski boards) were made earlier of wood and nowadays of composite material. Evolution of the world record in pole vault career is related to the transition to composite material for equipment, Tables 3 and 4 (data in tables based on Remond and Caron, 2020).

CMC Composites and Automotive Manufacturing

CMC composites in automotive manufacturing, are promising material because of their thermal stability. Corrosion resistant, light weight CMC components in brake technology, their current Status and Future Prospects of CMC Brake components and their manufacturing are presented in (Renz *et al.*, 2012).

Table 2 Aging of various material

	Resistance to traction, MPa	After 107 cycles fatigue MPa	Resistance to traction, MPa	After 107 cycles fatigue, MPa
Composites, carbon, isotropic	450	≈ 400	≈ 250	≈ 200
Alloys Aluminum	450	≈ 170	450	≈ 90

Note: Remond, Y., Caron, J.-F., 2020. Les matériaux composites dans le sport, Mediachimie, sport. Available at: https://www.mediachimie.org/sites.../chimie-sport_195.pdf.

Table 3 Vault pole records in time vs material

Material	Wood	Bamboo	Metal	Fiberglass
Year span	< 1900	1900–1940	1940–1960	1960–2000
Record [m] real ^a	3.1–3.7	3.7–4.7	4.7–5.2	5.2- over 6

^athis dependence could be presented by linear regression (Remond and Caron, 2020).

Table 4 The content of material in “fiberglass”

Component	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O ₃	B ₂ O ₃	Fe ₂ O ₃	TiO ₂
%	53–55	14–15	17–23	1	0.8	0–8	0.3	0.5

Note: Remond, Y., Caron, J.-F., 2020. Les matériaux composites dans le sport, Mediachimie, sport. Available at: http://www.mediachimie.org/sites.../chimie-sport_195.pdf.

Simulation of Interaction CO₂ Laser and Composite AlSi/SiCp

Using the proposed thermal model for laser-material interaction, simulations were made by program package Comsol Multi-physics 5.2 for composite type alloy AlSi/SiCp where vol. part of SiCp is 15%. Supposed dimension of sample for simulation were $15 \times 15 \times 3$ mm. CO₂ laser is chosen with 10.6 μm . Chosen diameter of the beam was 0.25 mm on the target. Physical and thermodynamical values for simulations were: density 2238 kg m^{-3} , thermal conductivity $k = 97.9 \text{ W/m K}$ and $C_p = 896 \text{ J/kg K}$.

First estimation was continuous (cw) action laser in the 1 s duration/exposition, by laser power 100 W.

Temperature distribution versus time in 100 ms, 300 ms, 500 ms, 750 ms and 1 s, respectively, are presented in the Figs. 3–7.

Simulations With CO₂ Laser in Pulse Regime With 5 Hz Repetition

For simulation the power was 100 W, and time for exposition was 1 s. The temperature distribution for 100 ms, 300 ms, 500 ms, 750 ms and 1 s are presented in Figs. 8–12.

Some Remarks About Modeling and Results

Subject of discussion could be the approach of modeling without considering the real pulse shape of CO₂ lasers in different working regimes. The above is presented only from the software point of view – in this case Comsol. More detailed modeling of laser CO₂ interaction with material and complex pulse is in (Srećković *et al.*, 2012b). Another approach considering software packages and simplifications is in (Kaluderović *et al.*, 2017; Srećković *et al.*, 2008).

Influence of microgeometry of the structure (Janicijević, 2011; Srećković *et al.*, 2015, 2017) is important for composite because of variety in their different types including matrix, fiber and powder particles (today nanoparticles also).

Porous media are treated, generally, as the mixture of solid and fluid phases. Therefore heat transfer is described by one equation and model of the composite based on equivalent heat conductivity. Thermodynamic balance is not suitable for very short pulses.

Statistical approaches and nonconventional/traditional approaches are connected to fractals (Mandelbrot, Hausdorff numbers, Hausdorff dimensions). Formalisms with length L and Euclidian geometry (area and volume), in various forms should be used. Hyperbolic heat conduction (HHP) and heat conductivity process, is valid. Newly developed generalizations have to be performed and they include recursion procedures, critical behavior of spin-continuum Gaussian based on translational and invariant lattices and fractals, respectively. Generally these complex formalisms are correlating with classical treatments.

Gaussian model on Sierpinsky carpet, Yang–Lee edge singularity, model with 2 Sierpinsky fractal lattice/gratings, renormalization of the group and percolation connections on Sierpinsky carpet, are in use instead of supercritical fluid on phase diagram, statistical theory boundary friction of atomic plane of the solid state in microstructure. (Damage could be treated in presence of lubricant layers).

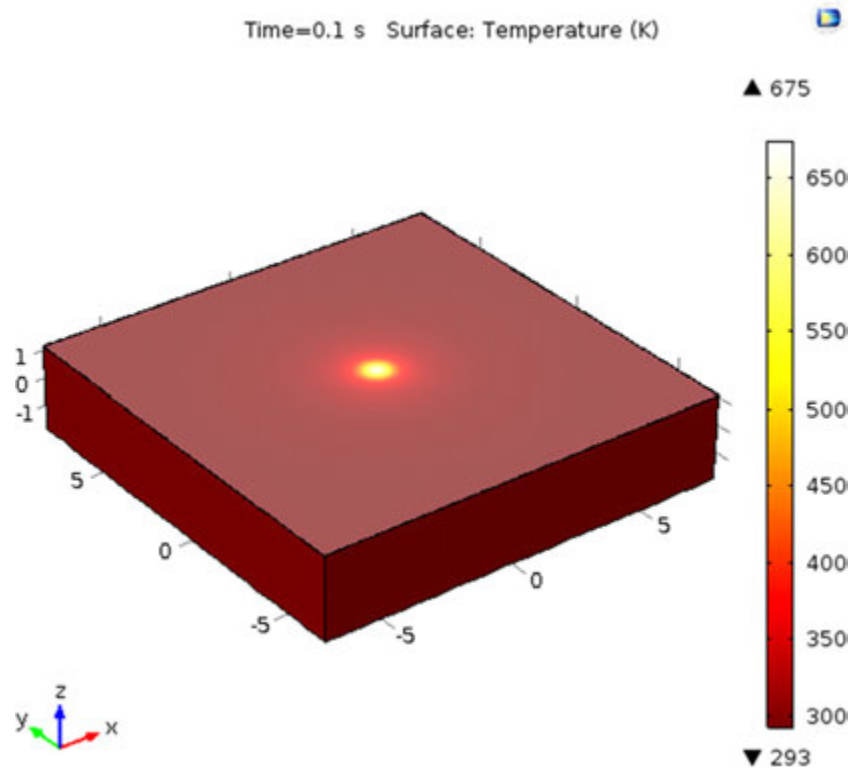


Fig. 3 Simulation of composite exposition to cw CO₂ laser beam in $t = 100$ ms.

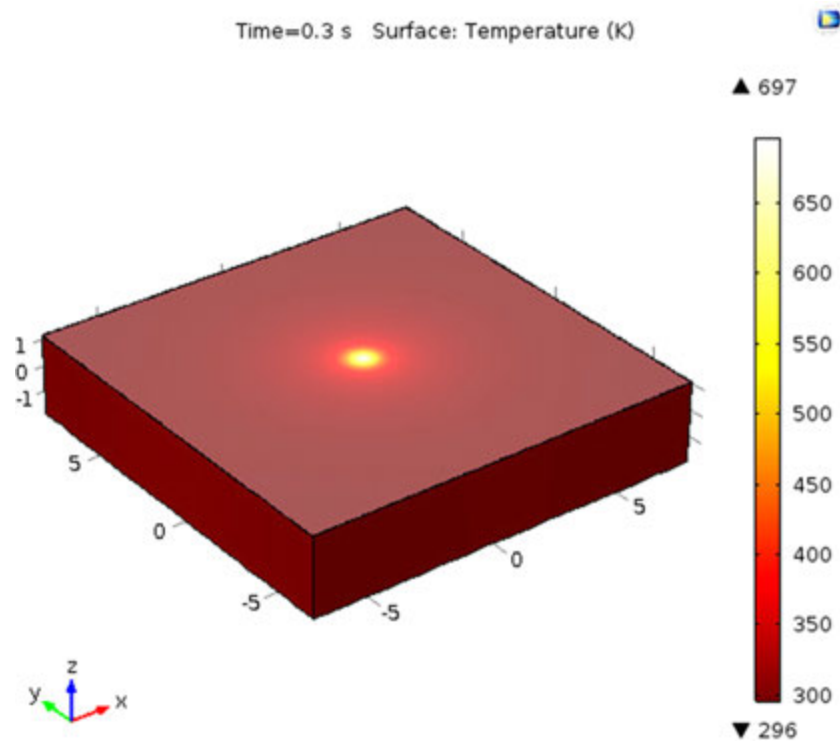


Fig. 4 Simulation of composite exposition to cw CO₂ laser beam in $t = 300$ ms.

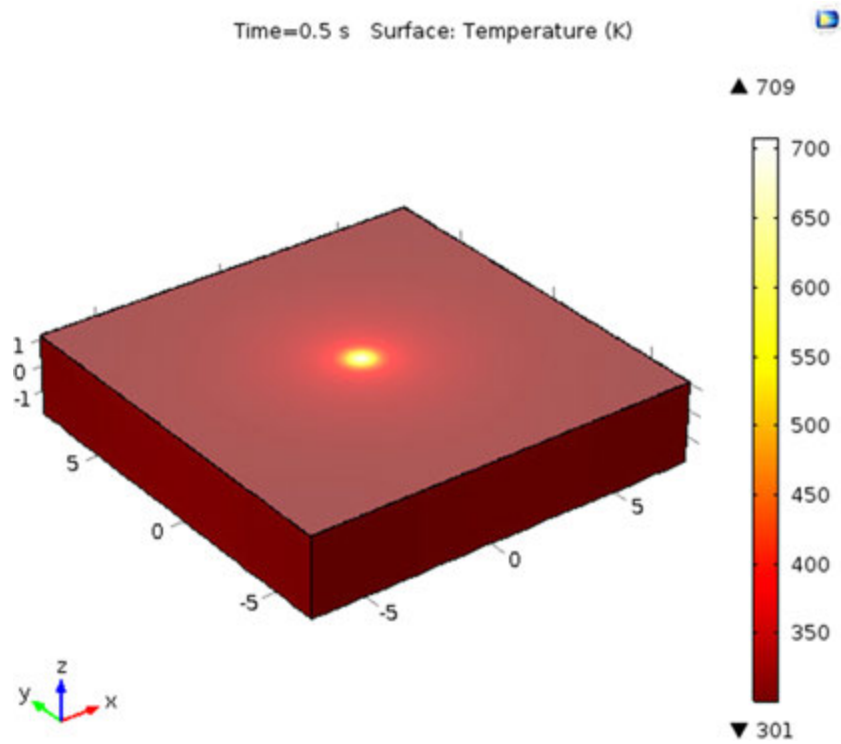


Fig. 5 Simulation of composite exposition to cw CO₂ laser beam in $t = 500$ ms.

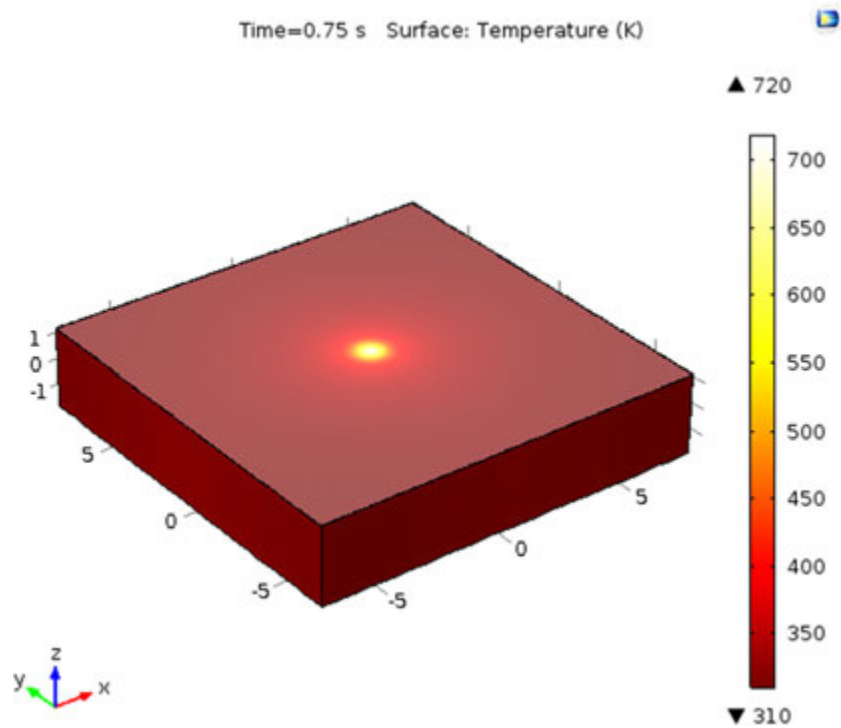


Fig. 6 Simulation of composite exposition to cw CO₂ laser beam in $t = 750$ ms.

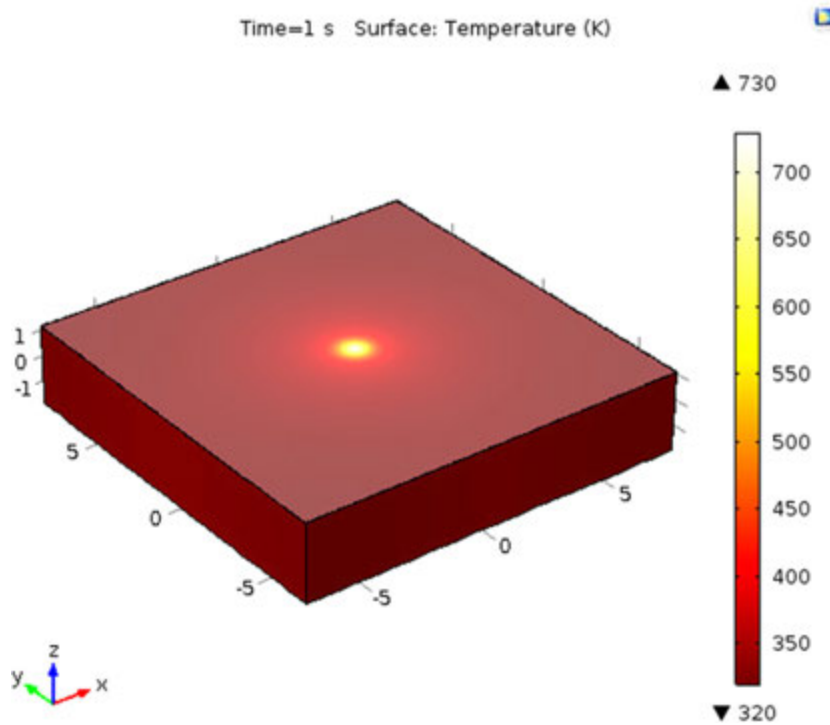


Fig. 7 Simulation of composite exposition to cw CO₂ laser beam in $t = 1$ s.

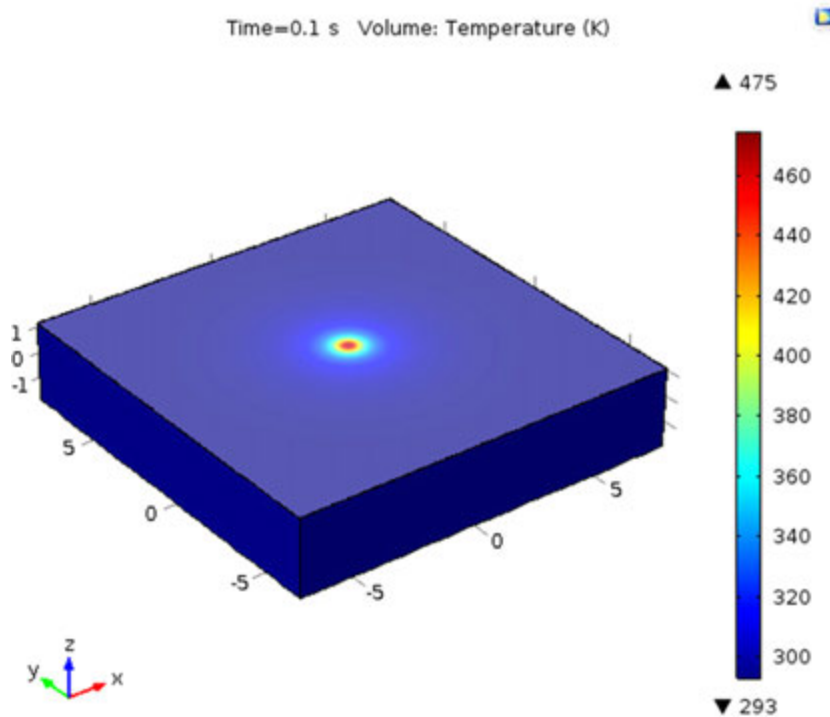


Fig. 8 Simulation of composite exposition to pulsed CO₂ laser beam (repetition 5 Hz) in $t = 100$ ms.

Laser and Material Interaction With an Emphasis on Laser Processing

Contemporary, material processing (machining) includes very different processes comprising: the required operation with needed damage, separation, but also joining, modulation, engraving, surface processes could be considered from many directions.

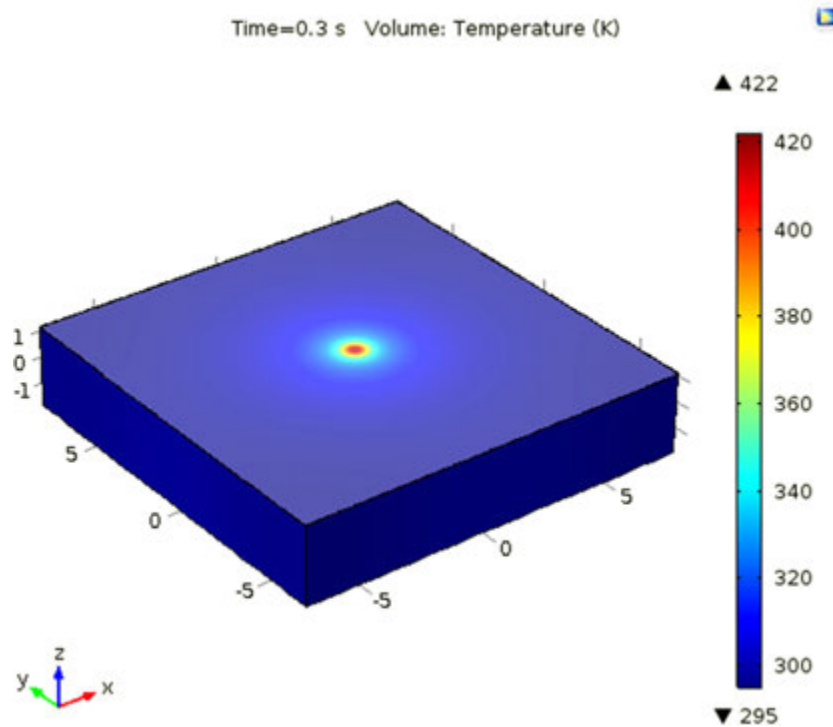


Fig. 9 Simulation of composite exposition to pulsed CO₂ laser beam (repetition 5 Hz) in $t = 300$ ms.

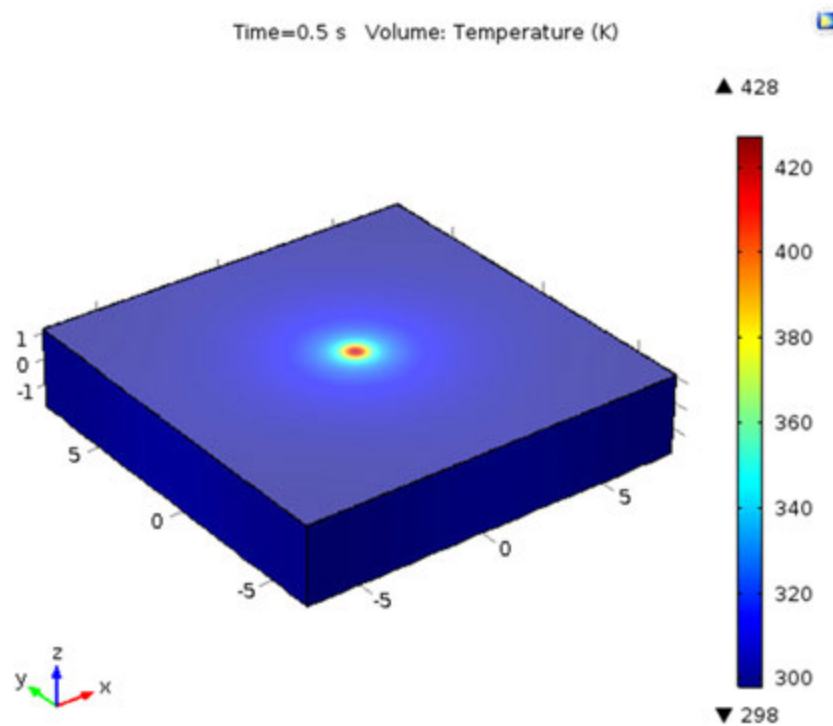


Fig. 10 Simulation of composite exposition to pulsed CO₂ laser beam (repetition 5 Hz) in $t = 500$ ms.

Generally, they are based on general statistical, thermodynamical theory of fracture, but fin the 70 years the specific laser/material interaction has been developed. In laser-material interaction, various known and unknown very complex processes can be found. Therefore they can be analyzed from different stand points: choice of the model, selection approximation, discussion about laser temporal action, possibility of plasma processes (breakdown, only modulation, transformation from the basic phases of material

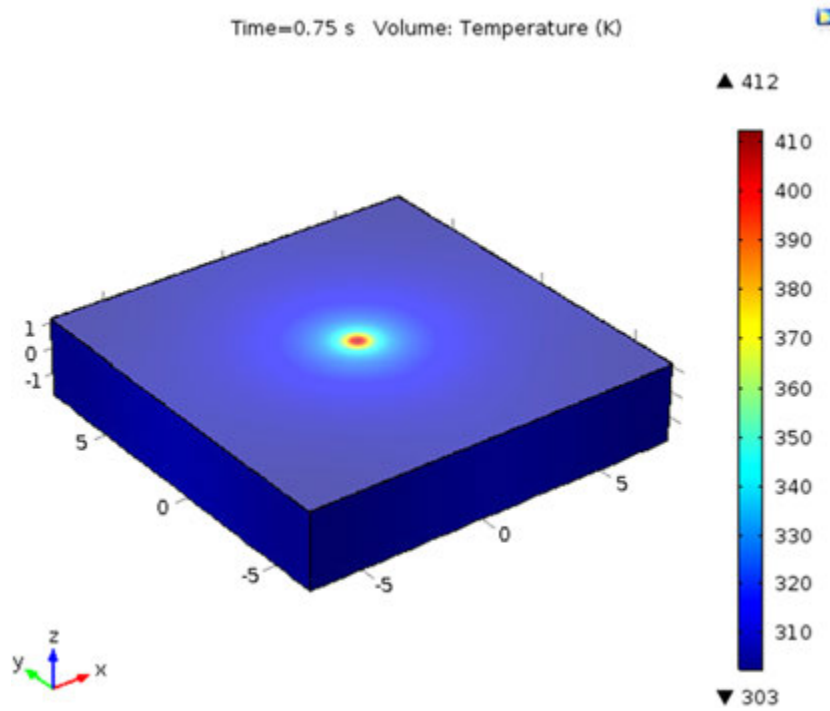


Fig. 11 Simulation of composite exposition to pulsed CO₂ laser beam (repetition 5 Hz) in $t = 750$ ms.

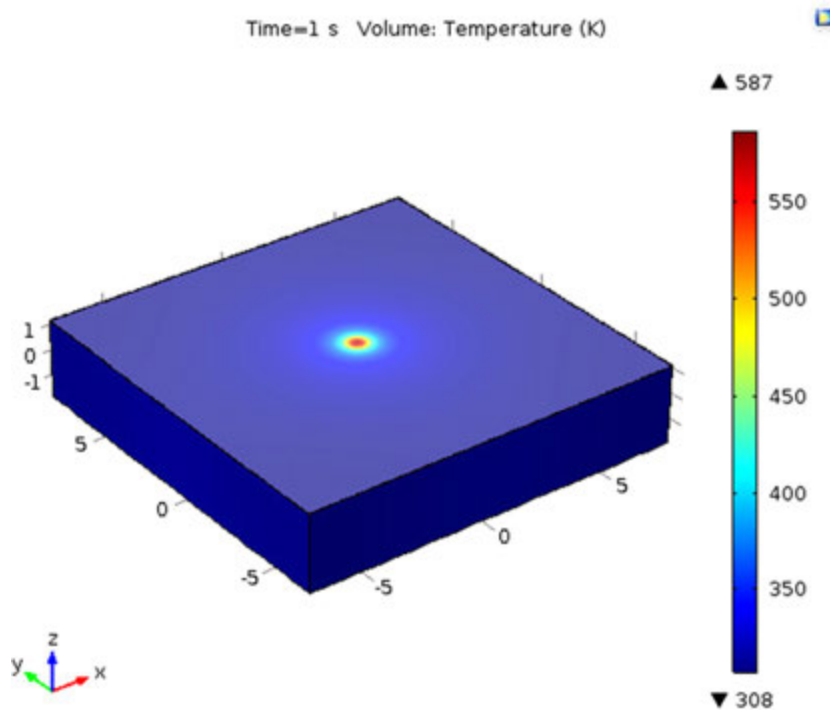


Fig. 12 Simulation of composite exposition to pulsed CO₂ laser beam (repetition 5 Hz) in $t = 1$ s.

up to crystal/amorphous, or further, changes in lattice, etc). Since composite are complex structures, even in the case of CMC composites, many of existing theories can be used in:

- (1) Calculation of temperature distribution,
- (2) Calculation of provoked stress,

- (3) Calculation of processes of material joining,
- (4) Calculation the processes of the material separation (cutting, drilling, engraving; that is all mentioned).
- (5) Evaluation of laser application in measuring methods that do not disturb the material, etc.

The theory should be valid in the wider range of needed parameters which can resolve and describe different mechanisms (dielectric, thermal breakdown, Brillouin breakdown, self-focusing, excitations of new nonlinear effects). The first approaches were: the model of thermal decomposition, gaseous dynamical model, bulk evaporation model, model of similarity, and many phenomenological models. The values of material's optical, acoustical, mechanical and thermodynamic parameters and the applied laser system parameters determine the range of the model's validity and the choice of practical criteria. The threshold in some cases could be the only object of research.

Thermal disintegration theory starts with equations:

$$\frac{\partial^2 T}{\partial^2 z} + \frac{v_0}{a} \frac{\partial T}{\partial z} = 0 \quad (1)$$

$$\lambda \left. \frac{\partial T}{\partial z} \right|_{z=0} = q - \rho \Delta H v_0 \quad (2)$$

$$\Delta H = \frac{2L_b - R_b T}{2} \quad (3)$$

where: H-denotes the difference of the specific enthalpies, L_b , R_b -evaporation heat and universal gaseous constants, a = temperature conductivity, $a = \lambda/\rho C$, ρ -density, C -specific heat, T -temperature, v_0 -sound velocity, for chosen geometry. The solution of the system of Eqs. (1–3) is given by:

$$T = T^* \exp(-zv_0/a). \quad (4)$$

Further including respective connections and appropriate considerations, transcendental equations are obtained:

$$e^p = K \frac{2p + 5}{2p + 1} \quad (5)$$

$$K = \frac{100S}{9\pi a \rho L_b} \quad (6)$$

where p^* -is normalized pressure, and constant S , close to the sound velocity in the material, under interaction. Note that laser dynamics should be also taken into account. For chosen cases with different laser pulse energy, power density and plasma temperature in the domain of gasodynamical models quantitative relations are calculated and analyzed (Srećković *et al.*, 1993, 2001a,b, 1998).

Introduction in the Interaction and Some Laser Damages of Various Composites

The knowledge of the properties of composite materials is very important for educational application particular in aircraft industry, as mentioned. At the down of the new millennia, a large number of composite materials were produced on the basis of two of more components.

Within the framework of these investigations the behavior of the composite was investigated during the interaction with focused and unfocused beams of the ruby laser.

The particular place was given to carbon based composite materials. The analyses for the possible state of stress and elasticity have been performed.

Fiber structures in composite are characterized by anisotropy of features. The necessary hardness of the material was obtained by orienting fibers in the direction of action of mains strains/loadings. The anisotropy of features is not shortcoming since it is possible to manufacture parts with distributions of mechanical properties corresponding to strain distribution tolerated by the material. The greatest application among composite on the basis of carbon fibers belong to the composites with polymerized epoxy resin (of use in aircraft industry, vehicle, shipbuilding, chemical industry, textile, mechanical industry, and civil engineering, too).

For the need of experiments (Ristić *et al.*, 1993) two types of composites/laminates were made: unidirectional composite of the carbon fibers epoxy resin with parallel fibers and composites with fibers under 30°. Samples were produced, starting from laminates with the processes of polymerization in the autoclave, in laboratory environment (Ristić *et al.*, 1993) using the original procedures. The pressure and the temperature were controlled with specific manufacturing technology. The mechanical characteristics of the composites before laser beam interaction are in Table 5.

Table 5 Some details for composite treated with ruby laser

No	Composite type	Tensile strength, R_m , MPa	Modulus plastic, E , GPa	Poisson's ratio μ
1	[0°] 16	1450	130	0.325
2	[30°]4s	230	6	0.725

Mechanisms and Effects of Laser Interaction With Composite Materials

Considering above mentioned in praxes, theories and our simulations, the processes of laser material interaction are complex phenomena, depending on series of factors: characteristics of the laser beam, physical and chemical properties of material and the ambient. Transfer of laser beam energy to the material, very often transformation in thermal energy, require high coupling coefficient. Optical and thermal characteristics of the material are of decisive significance for the interaction of laser-material. The composite on the basis of epoxy resin and graphite fibers have a high coefficient of the absorption; the reflection and transmission coefficients are negligible for wavelengths over 600 nm. From that point of view laser beams (ruby, $\text{Nd}^{3+}:\text{YAG}$, and CO_2) are suitable for the application. The thermal features of composites are important showing insulator performances. The matrix and armature differ considerably. It is indispensable to consider the effects of light scattering in material where fiber diameters are comparable with wavelength as well as diffraction phenomena. Apart from the structural weakening occurring due to surface heating, softening, melting and evaporation of material, bubbles, plasma phenomena, multi fold scattering, could be formed.

The shock waves appear when the great laser power density is applied. On the surface of the material a sudden local increase of the temperature occurs, provoking the evaporation of the material (at the speed of sound). Also, formed shock wave propagating through the material initiate destroying processes. In metals an additional effect appears. It is X radiation which can change the structure of the material. These effects are not expected in many composite materials but, for composite with metal matrix, with metal fiber, or powder, excitation is expected.

For each target material for laser beams detailed history of initial technology and aging in the moment when the interaction occurs should be presented (as well as the laser system details). Laser damages on chosen materials in various laser working regimes are presented in this study.

Investigation of the Possibilities of Ruby Laser Application in Composite Material Processing

Damages for various energies and number of repetitions were performed. Special attention was paid to define a nature of damage depending on material homogeneity as well as efficiency of applied ruby laser in manufacturing of aircrafts or missiles.

The experiments were realized under normal laboratory conditions: (Ristić *et al.*, 1993) normal atmospheric pressure and room temperature. Laser functioned in TEM₀₀ mode, in free generation regime, wavelength 694.3 nm, linearly polarized. The unfocused beam diameter was $D = 10$ mm, the divergence 5mrad. Pulse energy varied from 0.1 to 3.5 J and energy density 1.2 mJ/mm² and 0.286 mJ/mm². The intensity distribution was Gaussian and the pulse length 5 μs . The beam focusing is made by a lens with aperture 30 mm and the focusing length $f = 150$ mm. The lens had an antireflection layer corrected for spherical and chromatic aberrations. The sample and the lens were placed on a support with micrometric tuning enabling precise change of the geometry. Taking in account the laser beam width before focusing and geometric characteristics of the lens, the dimensions of the laser beam in the focus were defined (can be calculated). In the selected configuration, the surface on which laser beam is focused had diameter of 0.015 mm. The average density of the power was 740 J/mm² – 25 kJ/mm². Those are very high energy densities leading to the appearance of plasma and shock waves and creation of light effects. During those experiments for the mentioned composite, as well as, for other material (Srećković *et al.*, 1996) the area of the laser beam effects on composite was investigated using scanning electron microscope SEM (magnification 30–300 $\times$ were used). Therefore the structure of the composite can be analyzed as damaged and non damaged areas (fiber breakages).

The analyses and results show the following: The material changes provoked, by laser beam, can be of different forms: structure of materials, appearance of macro and micro cracks with the ejected material, the trace of melting or vaporization processes, etc. For composite material, primary interest is to determine the nature of changes in the damaging zone, the behavior of matrices and fibers/powder component. The depth of damage increases with energy density or repeated pulse regime. A large number of results, presented here, have shown interesting effects of laser beam to composite material of chosen type. Area of melting of the matrix on the surface and the area of the complete breakdown could be recognized and the perforation of the material, too.

Some experimental results of different targets and various laser types are presented in the following paragraphs. These are: those of interest in aircraft industry; some other carbon based composites, HAP and tooth, BCB composite, etc. PMMA materials with organic resin and Nd-Fe B magnetic powder are included only through references. For some material more details were shown, and for others only the results of the damage by laser beams and remarks.

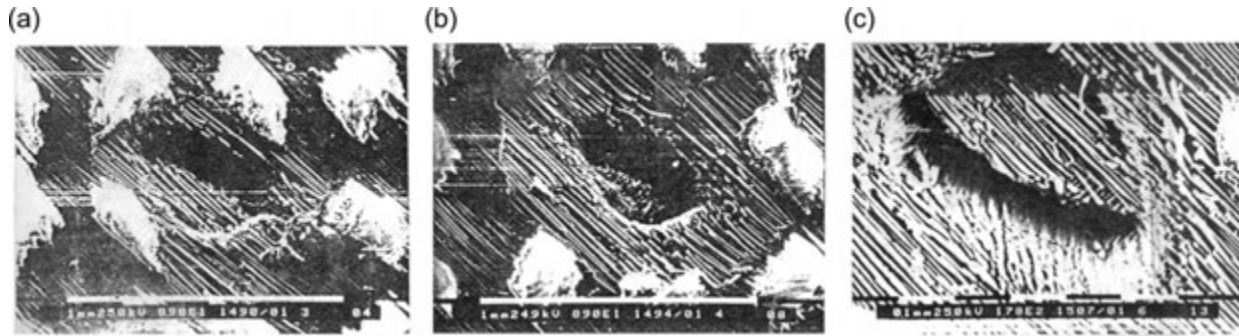


Fig. 13 Unidirectional fiber and damage: (a) $E = 0.7$ J; 89x; (b) $E = 1.1$ J, 1 pulse; (c) $E = 1.8$ J 1 pulse: 178x.

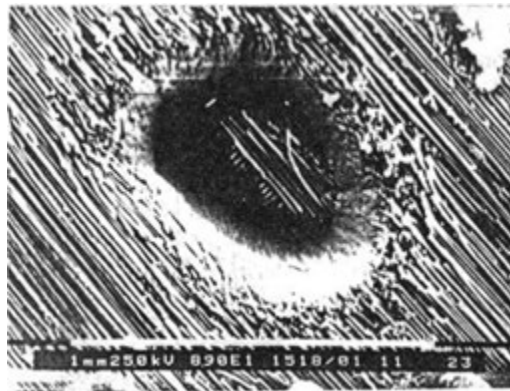


Fig. 14 Composites interaction with ruby laser $E = 3.5$ J, 5 pulses: 89x (Damage depth up to 6th layer).

The analyses and results for selected material/composite exposed to different laser beams show the following:

a) The results for composites type 1, which is of interest for aircraft

Selected SEM micrographs of the unidirectional and bidirectional composites described are presented in Fig. 13, depicting results of ruby laser interaction. In Fig. 13 are the laser damages of unidirectional composites with the magnification in experiments 24.2–300x, and laser pulse energy 0.32–3.5 J and in free generation mode, $t = 5 \mu\text{s}$.

For bidirectional composites with fibers (in configuration 30°), with working experimental parameters: $E_{\text{pulse}} = 3.5$ J, number of pulses in the same point was 4 to 6. The damage depth in the same point 5 pulses ($E_{\text{pulse}} = 3.5$ J) was 1.5 mm (Fig. 14).

The mechanism of interaction with *second type* (causally)- selected materials of this group is analyzed having in mind several developed theories (fracture theory, plasma interaction with materials, thermal models with phase transitions, fractal theory and similar). In this work, modeling of some laser operations (visible, IR, various pulse lengths), differing by several orders of magnitude, has been performed. Considering different approaches to the beam-material interaction observation and the ejected particles monitoring, some unsolved questions arose. Two different standing points of material observation: from damages and from ejected material, have shown differences of fundamental nature. Results have been analyzed from these points of view and compared to experimental results. In this work, the interaction of laser beams (of well known lasers, like $\text{Nd}^{3+}:\text{YAG}$, CO_2 , but also alexandrite and others) with optical materials (*in wider sense of view*) is reviewed. As an experimental part, some damages have been analyzed by light and electron microscopes, as well as EDX, confirming that material content changes or preservation. The shapes of damages depend on the laser working regime: pulse width, mono or multi-pulse, Q switch or free generation mode-expositions. Cumulative effects are the subject of investigation by many authors. In the terminology of optical damages, there are precisely defined protocols for laser damage, but they differ in both investigation types and the damage term application. The results on various materials could enable analyses of several types including the data on the source itself, materials resistance to optical beams, and research of other developed fatigue tests as well. For some approaches, calculations which represent numerical implementation for given geometries and chosen pulse shapes, have been performed. Besides that, interpretations which would be commonly deduced, based on the models of obtained record processing, has been given. In Fig. 15 and Table 6, the results, obtained for samples of Cu and different percentage of Al_2O_3 , and its particle size has given treated with laser + 3.5%: (alexandrite, etc). Their characteristics are studied through the measurement of electrical resistance, starting from pure Cu. Besides that particles of alumina were changed and the influence of their size found on electrical performances, was found. Electrical performances generally indicate the trend of changes of other parameters, also, laser interaction depends on the size of alumina.

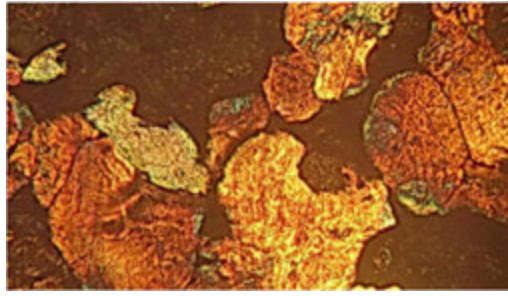


Fig. 15 Cu + 3.5%: Al₂O₃ (Sample 2) showing the area of dark/treated zone, analyzed by light microscope. Reproduced from Sreckovic, M., Druzijanic, D., Janicijevic, A., Janicijevic, M., Bugarinovic, A., *et al.*, 2017. Analytical and experimental approach to laser interaction with various materials. In: Proceedings of the Conference on Contemporary Materials, 9–10.11. pp. 123–149.

Table 6 Samples of Cu with Al₂O₃

Sample	Resistance mΩ	Average alumina particle size, nm
Cu	27	–
Cu + 1.9 wt%: Al ₂ O ₃	25	Nano (60)
Cu + 4.9 wt%: Al ₂ O ₃	30	Nano (60)
Cu + 3.5 wt%: Al ₂ O ₃ /10 h	17	Nano (750)

Note: In: Bass, M., (Ed.), 1983. Laser Materials Processing. Amsterdam: North Holland.

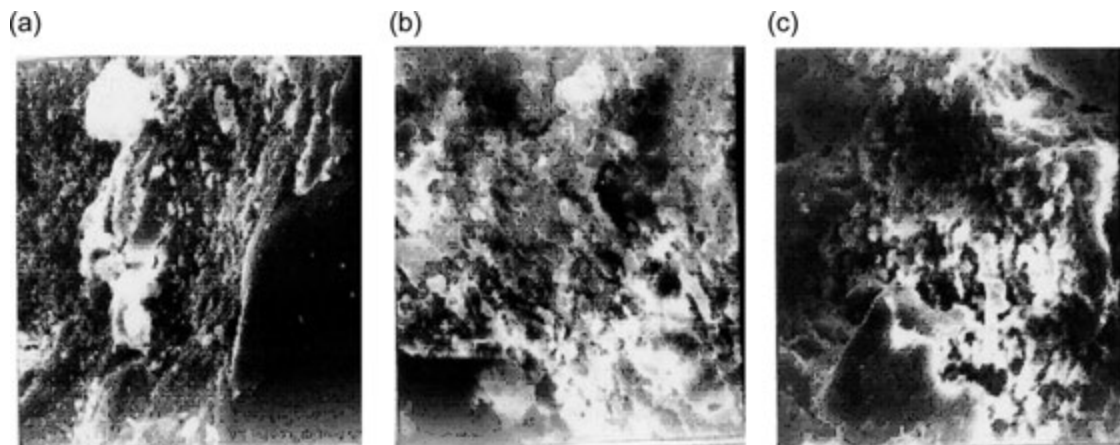


Fig. 16 Tooth and HAp damaged by Nd³⁺:YAG: (a) tooth E = 250 mJ. Q switch, SEM 396x (b) HAp white sample, the same exposition as tooth SEM 396x (c) Details for tooth SEM 660x, Q switch, bottom of the crater provoked in tooth.

Biomaterial Composite and Laser Action

Composite biomaterials could be of following types: metal/metal, metal/ceramics, metal/polymer, ceramics/ceramics and polymer/polymer. Composited can be based on powder or fibers.

The micrographs of the selected biomaterials HAp and tooth are presented in Fig. 16. Ceramics/ceramic composite close to bones and some tissue are: TCP/HAp, HAp/Al₂O₃, HAp/SiO₂, HAp with Al₂O₃. It could be of interest to compare previous Cu + Alumina to Hap + Alumina, in case of laser exposition.

Ceramics/polymer composites are mechanically the closest to the natural bone. The problems are toxicity of polymers and its aging unsteadiness. Between the changing surface methods of bioprophetic material (including bioglass), various laser exposition doses could be successful.

Silk Samples

Are presented in following Fig. 17, showing the damages made by ruby and Nd³⁺:YAG laser.

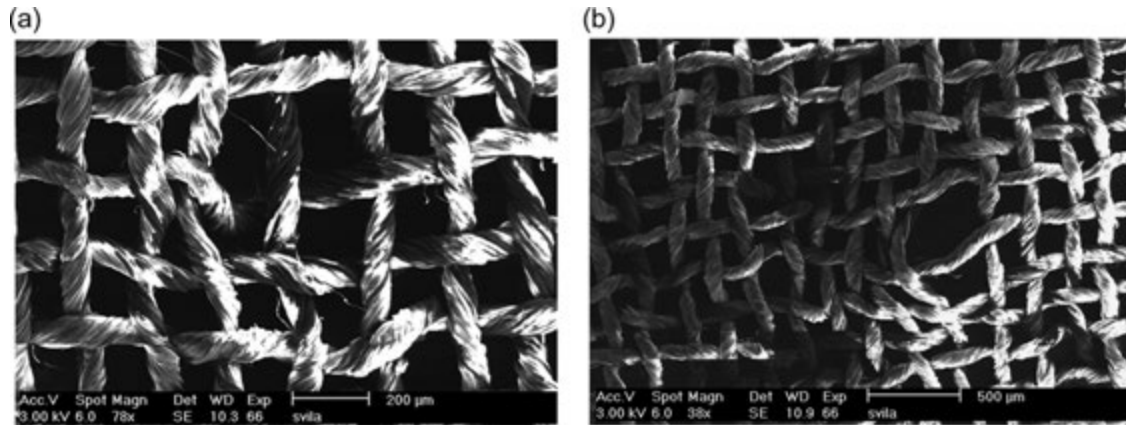


Fig. 17 Silk, (a) Ruby laser, SEM micrograph, 78x, $E = 0.3\text{--}2\text{ J}$, $\tau = 30\text{ ns}$, 1 pulse, General damage view and (b) Nd^{3+} : laser, $1.064\text{ }\mu\text{m}$, SEM micrograph, 38x, $E = 35\text{ m}$, $\tau = 20\text{ ns}$, 10 pulses, General damage view.

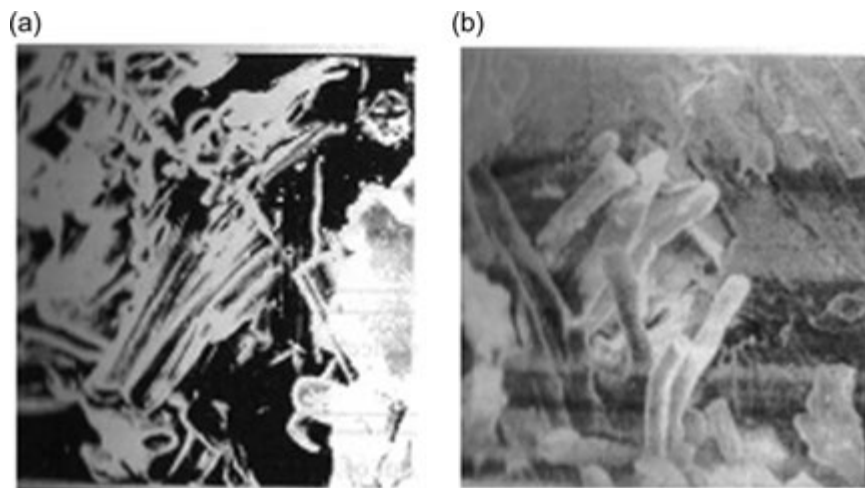


Fig. 18 Damages of composite bakelite –type A, treated with ruby laser $E = 2\text{ J}$, 30 ns , (a) wall of the damage, SEM 198x (b) the center of damage SEM 1320x.

Carbon Based Composites

Are studied through laser material interaction (Kaluderović *et al.*, 2017; Janicijević, 2011; Srećković *et al.*, 2015, 2001a, 2012a, 2004a) ImageJ was used to interpret and to quantify the intensities of interaction based on SEM and light microscope analysis.

Bakelite Material

Of two types are exposed to ruby and Nd^{3+} :YAG lasers Figs. 18–20. The comparison with other presented material is further possible (Srećković *et al.*, 1998, 2012a, 2004a). The data on thermal conductivity for this material was obtained by laser pulse methods (Srećković *et al.*, 1998) and simulations of interaction are in process.

BaTiO_3

Ceramics is, vastly studied and used, in electronics/microelectronics, pure as well as with addition of Ag, Au, and lately with La and Sb (Vijatović, 2010; Lazarević *et al.*, 2010; Milošević, 2018) of. Its role as BaTiO_3 , doped with 0.5 mol% of La and Sb and sintered at different conditions was investigated through XRD analysis, Raman, and IR spectroscopy. Nanopowder was used with detailed investigation of grain size distribution, and morphology of sintered samples was determined using SAM. Laser interaction with this type of material was subject of investigation by young researchers, too, giving the data with two laser types as well as simulation of laser induced temperature distribution.

The investigations of laser beam-composites are today very large (Grabowski *et al.*, 2008; Vijatović, 2010; Lazarević *et al.*, 2010; Milošević, 2018; Srećković *et al.*, 2004b; Polić - Radovanović *et al.*, 2004; Grujić *et al.*, 2010; Pavlović *et al.*, 2011). Some of them

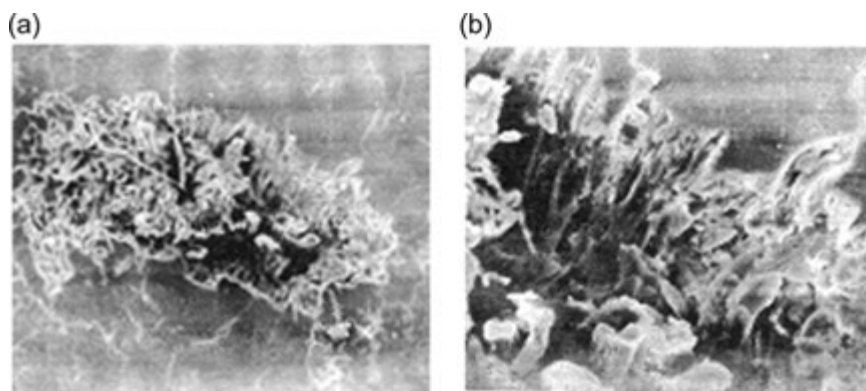


Fig. 19 Damages of composite type A, treated with Nd^{3+} :YAG laser, $E = 250 \text{ mJ}$, 15 ns , (a) SEM 66x, (b) surface of the material and crater wall; SEM 198x.

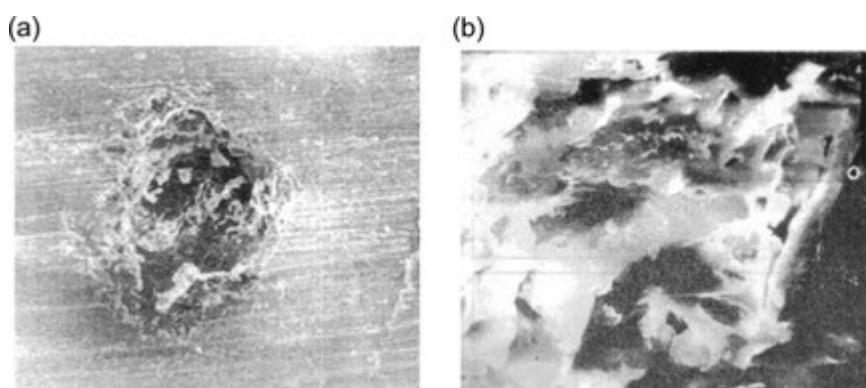


Fig. 20 Damages of composite type B, treated with Nd^{3+} :YAG laser, $E = 250 \text{ mJ}$, 15 ns , (a) damage, SEM 53x (b) damage wall SEM 660x.

search, identify physical chemical and other characteristics when focused beam acts on metal matrix composites reinforced with SiC particles.

BCB Disiloxane Bisbenzocyclobutene Material

In the form of thin films are investigated in interaction of nuclear particles and laser beams, choosing different working conditions. Damages were close to ideal circles, and quantitatively light microscope micrographs were further studied using Image. The changes of damage shape were quantified in the transition from circle to other shapes (Ivanović *et al.*, 2013; Veselinovi, 2009; Đurđević, 2009).

They have the unique combination of properties induced by stable aromatic, and reactive, strained cyclobutene rings and they have low dielectric constant. BCB based dielectric polymers have applications in micro and optoelectronics, as interlayer dielectric materials, wafer-level adhesive bonding materials, gate materials for organic field effect transistors, and as the materials for biosensors components. With low optical losses, high transparency, up to $1.7 \mu\text{m}$, and refractive index ($n = 1.549$ at $\lambda = 838 \text{ nm}$) they are dielectric materials for optical applications in integrated circuits. Trends for enhancement BCB performances show increase. Uncured and cured BCB films ($2 \mu\text{m}$), spin coated on glass/into surface, were studied using light and AFM microscopes, IR and Raman spectroscopies (Ivanović *et al.*, 2013).

Discussion and Conclusion

Generally, the acquired data using microscopy and other methods performed on material are not in coherency if the measurement of ejected material are made and this is one of important questions for further discussion, but it is not only the question of losses. This means that two directions of research are observed both theoretically and practically. Simply said, when only the ejected material from the target is observed (charged and uncharged particles, according to their distribution, process temperatures' investigation does not provide the same data as the study of target material damage). Or, to put it mildly, there is a need to improve both directions of research along with the search for harmonization of results, further development of theories and the

like. An expression has been used that is expressed almost in such a manner in the literature. That is why it is insisted on a more detailed experimental descriptions and, if possible, the application of more techniques in the experimentation process.

The detailed description of process requires the derivation of parameter for a large number of experiments and controlling a large number of parameters in experiments i.e., the measurement of temperature in several points in the direction surrounding the domain of interaction, the switching on/off the fast camera for recording the process, automatic processing of the domain of action including the precise dimensioning, spectral analysis, fast camera system, etc. The hitherto results have shown the composite material have excellent coupling with ruby laser and the radiation on applied wavelength can be used with success in composite processing. A small number of undesired effects occur on a narrow domain, i.e., showing good efficiency of processing. The investigation will englobe some question: structural analysis and the analysis of mechanical characteristics of the composite in order to find out possible changes as a consequence of the action of the laser beam. Apart from the composite material, the one based on the epoxy resin has been developed and employed in previous years.

Old composite materials (bricks/concrete) underwent many changes and still represent the object of investigations, viewed from the fracture physics and mechanics. The fracture and the damage behavior need to be better understood, as a multiscale phenomena. The fracture resistance was studied in the past by the law of mixture when the most brittle element fails. The trend was that the best specific fracture resistance would be achieved by the highest possible volume fraction of the reinforcement (Kelly model, asymmetrical finite elements model) where these theories provide a good insight in the damage of various mechanisms with (or without) reinforcement. The influence of interphase is important. Local fluctuations in the volume fraction or in alignment of fiber play and have essential role. The probability of failure of a volume element is dependent on the distribution of microstructure elements (Taplin *et al.*, 1992).

The laser role in composite processing and measurement/diagnosis is proved to be very important as in praxis as well as in theory. Special role of laser technique is in changing material surface to be more acceptable to humans as recipients of prostheses/implants (Raković and Uskoković, 2010).

Many simple formulas for material destruction by laser beams are with mechanical moduli, Poisson number in macroscopic or microscopic formalisms having molecular/atomic data.

Fracture of fiber reinforced composites and fracture of particle reinforced composites use various theories and computed support (program packages). The detailed study of composite and the results of laser exposition could be obtained by formalisms with Mueller matrix and ellipsometry. The performances of the sizes and shapes of metal nanoparticles have been analyzed through laser scattering. Note that other laser types could be used in production of powder.

Counting all of techniques that could be of interest for analyses/study influence of laser on material in general, the list grows exponentially. For magnetic material it should be used SQUID, XRD, TGA (thermogravimetric analyses, magnetooptical and electrooptic effects in relation to glass; or transparent plastics). (New titles of effect appear - MOKa, etc). If complementary techniques are used, commenting should be carefully done, due to different frequency range where the measurement occur and therefore, if dispersion (acoustic/optic) are large, a focus should be on these measurements. Relationship laser-cultural heritage –biosciences-composites should be the object of discussion, not without the inclusion of laser processing and measuring techniques. The point is that the laser technique has long been involved in all these areas, in which there is a lot of space for composites, both for diagnostic purposes and for the purposes of processing/restoration, making prostheses, removing age-related deposits. Various material or tissue equivalent materials or material with magnetic, dielectric, or other performances and at the end nanoscience could be followed through composite (Pelemiš, 2010; Pelemiš *et al.*, 2009; Vučenović *et al.*, 2010; Jevtić *et al.*, 2015; Raković and Uskoković, 2010; Pelemis, 2006).

Some remarks are:

- (1) To enhance efficiency of machining, attention should be paid to the polarization state of the laser (change); if material is anisotropic (being the case with composite) it is important to control processes of cutting, and beam polarization, geometry of sample positioning. Other way is to apply CAS semi transparency circular polarizations crystals, multilayer reflector.
- (2) The evaluation of laser beam interaction with the material CMC, and their optical, thermodynamic and other properties is complex tasks. Depending on the energy domain involved, this could be connected to the other facts of interaction. Therefore it has to be clear what we will: -analyses of responses of particular effects about the performed interactions -analyses of other field characterized by chosen analyses -analyses of the need and sufficiency of particular effects for gathering the necessary initial data for the estimation of final interaction effects which would confirm some of the developed models.

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Investigations for Performance Analysis of Ceramic Composites for Bearing Applications

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Introduction

A bearing is a mechanical element which converts one motion into another motion and reduces friction between the moving machine elements. There are various types of bearings like radial bearings, thrust bearings according to type of load they have to support and sliding contact bearing, rolling contact bearings according to their contact nature (Harsha, 2006). In sliding contact bearings the sliding action takes place along the contact surfaces between the moving machine element and fixed machine element. The sliding contact bearing is also called plain bearings or sleeve bearings. In rolling contact bearings, the steel balls or rollers are introduced between the moving machine element and fixed machine elements. The balls serve rolling friction at two points for every ball or roller (Tung and McMillan, 2004).

Metal alloys are generally used in applications where wear resistance properties of materials are required as they can be easily machined, ground or forged for various wear resistant parts that have properties different from ceramics (Ezugwu *et al.*, 2003). Although, metals have high toughness but low strength, low hardness and wear resistance properties than ceramics.

Ceramics have high thermal resistance; high hot strength and very good wear resistance properties but have low thermal shock resistance. Thermal shock is basically a function of thermal expansion and thermal conductivity. In last 10 years lot of work has been reported to overcome the thermal shock. One of the solutions is found in composite materials. As an example aluminum oxide nano-fiber can improve the ductility of ceramic metal composites, keeping Young's modulus high while increasing creep resistance and decreasing brittleness (Das and Balla, 2015).

One of the methods for creating ceramic composites is mixing nonmetallic fibers with a ceramic matrix and sintering the component in a mold or supporting structure (Hammel *et al.*, 2014). The chemical vapour infiltration technology is attractive method to produce fiber – reinforced ceramic matrix composites using this technique strong and tough composites can be prepared with good corrosion, erosion, and wear resistance properties (Lazzeri, 2012). The addition of Al-6%Si alloy reinforcement in ceramics increases the linear shrinkage, strength and impact energy but density, porosity and hardness decreases (Aigbodion *et al.*, 2010).

For making power transmitting elements which are under continuous loading conditions Al-SiC metal-matrix composite can be used which possesses high strength, high stiffness, thermal stability at elevated temperatures, high corrosion and wear resistance and more fatigue life (Pawar and Utpat, 2014). Addition of SiC weight percentage in aluminum based composite material increases the micro-hardness and compressive strength (Jeevan *et al.*, 2012)). The strength of mullite-SiC ceramic composite depends upon the phase composition, relative density and the percentage addition of SiC. Good mechanical properties of ceramic composite can be obtained with 20% wt. addition of SiC (Akpınar *et al.*, 2012). The strength and toughness of mullite-SiC composites possesses higher strength and toughness as compared to monolithic mullite. Flexural strength varies from 646 to 855 MPa of composite as compared to 202 MPa for monolithic mullite (Singh and Gaddipati, 1988). Sintered mullite-SiC ceramic composite possesses good crack healing ability and crack-healed specimens have higher static and fatigue strengths than the normal specimens (Ando *et al.*, 2001). The literature review highlights that some studies has been reported on the improvement of mechanical and tribological properties of ceramic matrix composite materials but very less has been reported for improving properties of sleeve bearing by using ceramic metal matrix composite. This is important from process view point as because in bearing applications, one has to make tight balance between the properties of bearing material and moving element like shaft. In the present study, an attempt has been made to prepare mullite and SiC ceramic matrix composite material by using powder metallurgy technique to improve the properties of material which can be used for making sleeve bearings.

Materials and Methods

The ceramic matrix material mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) in powder form was procured from local market (Sigma Aldrich Company, Bangalore, India) and SiC powder was procured from Central Drug House, New Delhi, India. In order to make ceramic matrix composite both the powders were mixed with binder polyvinyl alcohol (PVA) in laboratory ball mill (see Fig. 1). Initially mullite powder 90% (by weight), SiC 10% (by weight) was mixed with PVA binder 5% (by weight) in ball mill for 8 h for making homogeneous mixture.

The homogeneous mixture thus prepared was compacted on hydraulic press for making green compact (see Fig. 2). The mixture was pressed in die with hydraulic press at 220 MPa load for making green compact samples.

The green compact ceramic composites were processed further for microwave sintering. Three samples were sintered under different conditions as per Table 1 by using 2.45 Hz microwave sintering furnace (see Fig. 3). Based upon different input conditions set as per Table 1, Fig. 4 shows finally procured sintered samples.

After sintering, porosity and average grain size of sintered samples was checked. To check porosity and grain size samples were observed with metallurgical microscope supported with image analyzing software for surface image of samples (see Fig. 5). Based upon Table 1, Table 2 shows results of porosity and grain size.

For establishing the properties of the ceramic matrix composite wear test was performed on pin on disc apparatus (Tribometer) as shown in Fig. 6. Table 3 shows observations of wear properties.

Table 3 outlines that no significant wear was observed in all the samples hence the composite matrix possesses good wear properties. For establishing high temperature application of ceramic matrix composite differential scanning calorimetry (DSC) analysis was performed (see Fig. 7) for three repeated cycles up to 400°C. Based on Fig. 7, Table 4 shows the results of energy absorbed per unit gm by ceramic matrix composite.

As observed from Fig. 7 and Table 4, it is clear that the sample 1 (which was heated to 1500°C) has high thermal stability (required for the bearing material working at high temperature) as compare to sample 2 and sample 3, which were sintered to 1550°C and 1600°C respectively.



Fig. 1 Ball mill (3D view used in present study).



Fig. 2 Green compact sample prepared on hydraulic press.

Table 1 Different conditions set for sintering process during pilot experimentation

Sample no.	Composition	Sintering temperature	Sintering atmosphere
1	90% Mullite, 10% SiC	1500°C	Ambient air
2	90% Mullite, 10% SiC	1550°C	Inert gas
3	90% Mullite, 10% SiC	1600°C	Inert gas



Fig. 3 Microwave sintering furnace.



Fig. 4 Sintered samples.

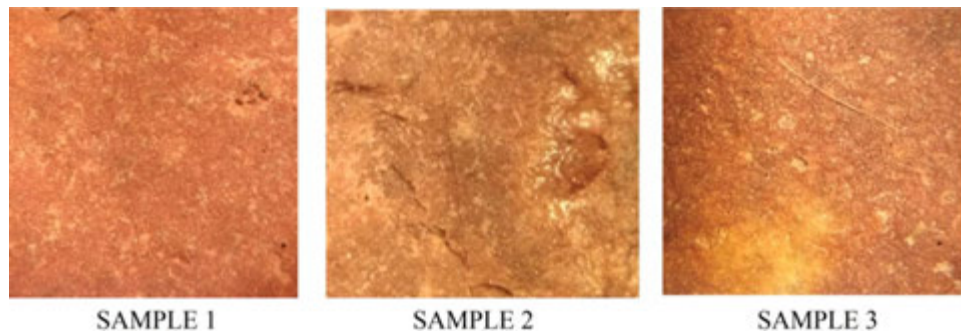


Fig. 5 Surface image using metallurgical microscope (at X100).

Table 2 Results for Porosity and Grain size

Sample no.	Porosity	Avg. grain size
1	86.25%	0.2581
2	94.9%	0.2581
3	84.16%	0.2581



Fig. 6 Pin on disc apparatus.

Table 3 Observations for wear on pin on disc setup

Sample no.	Load (kg)	Time (min)	Speed (rpm)	Track Dia. (mm)	Wear (μm)	Frictional force (N)
1	5	25	300	80	86	14.3
2	5	25	300	80	87	14.4
3	5	25	300	80	126	8.5

Discussion on Case Study and Process Flow Chart

In the present case study, mullite powder 90% (by weight), SiC 10% (by weight) with PVA binder 5% (by weight) has been initially processed on ball mill, followed by preparation of green on hydraulic press and sintering in microwave. Based upon [Fig. 5](#) and [Table 2](#), it has been ascertained that uniform grain size has been achieved with high surface porosity. This high surface porosity is really appreciable in bearing applications as more quantity of lubricant (as film) can be accommodated. The results of the wear analysis ([Table 3](#)) outlined very small/negligible wear; hence make this route acceptable for bearing applications. Finally the DSC analysis outlined that energy absorbed per unit gm in case of sample 1 is more than as compared to sample 2 and 3 (see [Table 4](#) and [Fig. 7](#)). Further there was no thermal deformation up to 400°C. Hence the proposed ceramic matrix composite can be used for high temperature applications. The results are in line with the observations made by other investigators ([Pawaskar and Prasad, 2014](#)). The proposed process flow chart for performance analysis of ceramic composites in bearing applications is shown in [Fig. 8](#).

For ascertaining the high temperature bearing applications, further studies may be conducted on lubricant film thickness under different loading conditions on test rig. Finally for preparing the industrial standard for the proposed route, study needs to be conducted (by following a design of experiment technique) with different levels of mullite, SiC proportion/composition, different pressure variation while preparing the green sample, temperature and inert gas variation in microwave sintering furnace.

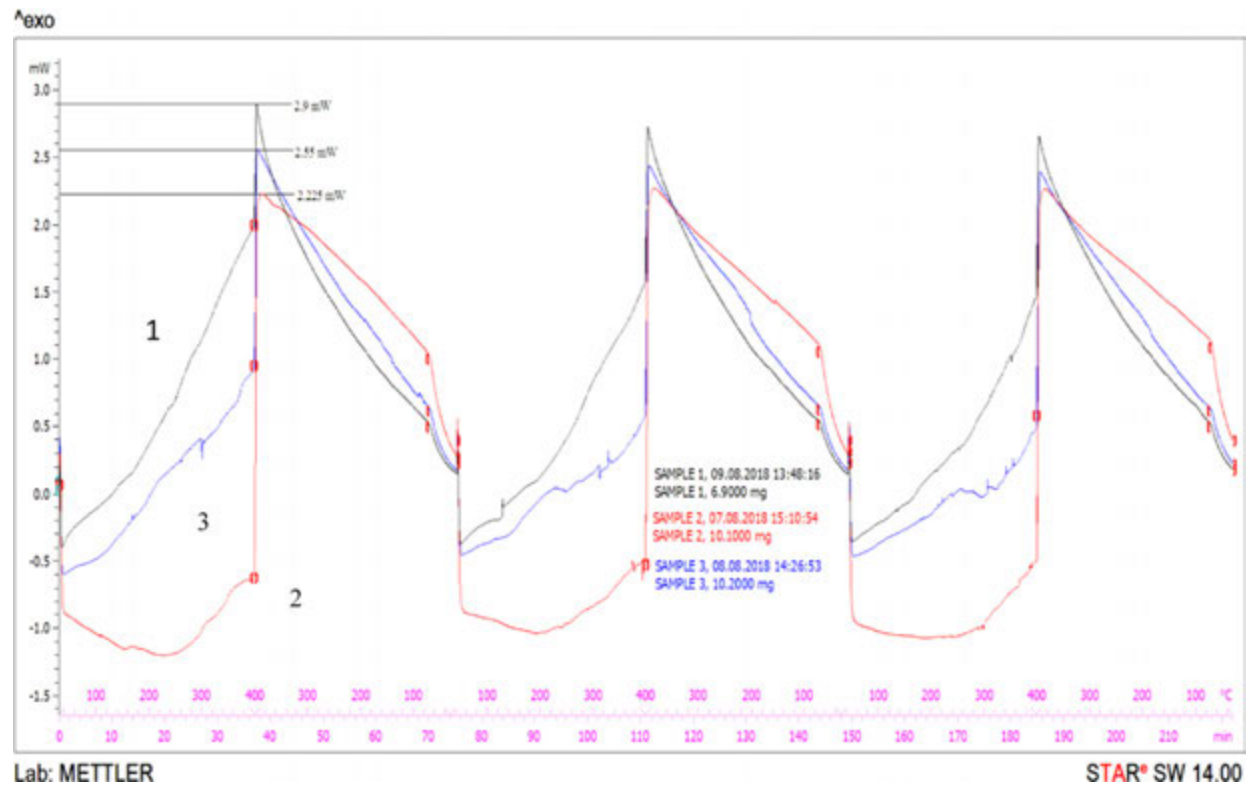


Fig. 7 DSC curves for the three samples (as per Table 1).

Table 4 Energy absorbed per unit gm (by the prepared samples as per Table 1)

Sample no.	Mass of sample (mg)	Total energy absorbed (mW)	Energy absorbed per unit gm (mW)
1	6.9	2.9	0.420
2	10.1	2.225	0.220
3	10.2	2.5	0.245

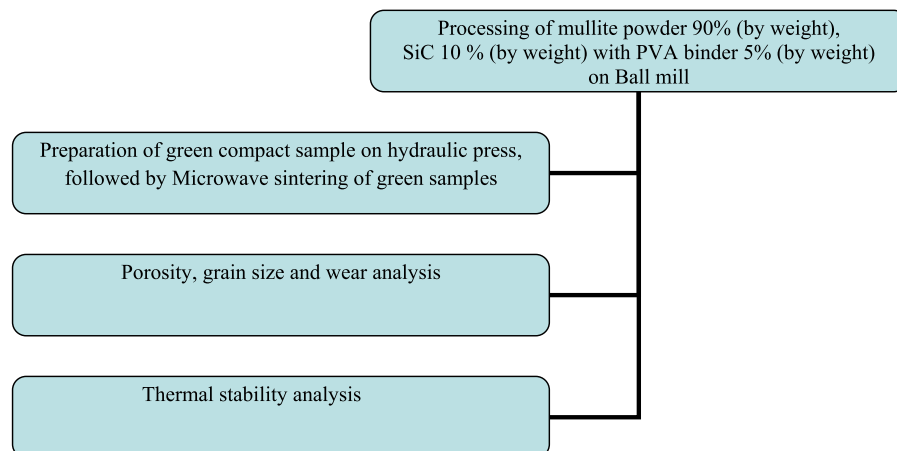


Fig. 8 Process flow chart for preparation of sleeve bearing (by proposed route).

Conclusions

Following are the conclusions from the present study:

- (1) The mullite and SiC based ceramic matrix composite has been successfully prepared by microwave sintering process. It has been observed that ceramic matrix composite possesses good wear resistance properties.
- (2) Further photo-micrographic analysis outlines that mullite and SiC based composites are suitable for sleeve bearing as its porosity is very good which is required for self lubrication. Based upon DSC analysis, it has been ascertained that mullite and SiC based composites are thermally stable up to 400°C, when they are sintered to 1500°C.

Acknowledgement

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Modeling of Mechanical Behaviour of Fiber Reinforced Composites

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Introduction

Throughout history, people have been inspired by natural materials to produce tools, weapons and energy efficient buildings. There is evidence that the Mesopotamian used straw to strengthen mud bricks and Egyptians had used plywood as moisture protection, thermal insulation and for achieving the advanced stiffness. During medieval swords and armour were made by forging several layers of different materials (Jones, 1999). At the turn of the two centuries, the nineteenth and twentieth, advances in chemistry led to development of plastics such as vinyl, polystyrene, phenolic. In 1935, Owens Corning introduced the first fiberglass, which combined with a plastic polymer produced strong lightweight material. Since the beginning of the application of FRC in the aerospace industry in order to reduce weight replacing several metallic parts amount of composite materials used in airplanes raised up to 50% in Boeing 787 (Holley, 2013). Development in the second half of the 20th century led to improvement in of fiber production, with engagement of aramid fibers, known as Kevlar, as well as high-strength carbon fibers that replace steel. The global production of concrete, the most common composite in the world, is 16 billion metric tons in 2013 (Ashby, 2013). Lately, nanocomposites reinforced with nanofibers (Saba *et al.*, 2019) or carbon nanotubes (Ates *et al.*, 2017) are gaining more attention from academic and industries. There are natural and man made composites. Since the total share of natural composites is modest, word composites usually refers to man made composites. Well known examples of natural composites are wood (cellulose fibers bound by lignin matrix), bone (stiff hydroxyapatite in a soft organic collagen matrix), granite (granular composite of quartz, feldspar and mica). Man made composites are plywood, concrete, fiber reinforced plastics, carbon-epoxy, polyester, cement etc. Composites are an ideal solution in areas where, due to reduced consumption, low weight with high specific strength and stiffness, or wear and temperature resistance are required, such as aerospace (Cavalier *et al.*, 2006), automotive (AL-Oqla and Sapuan, 2014), extreme sports (Ullah *et al.*, 2015) or medicine (Park *et al.*, 2017). The usage of fibers as reinforcement, caused by superior mechanical properties, have been rapidly growing during last few decades. With the increase in polymers and fibers manufacturing, the presence of composites such as polyester, fiberglass, epoxy-carbon, as well as combinations of metals and polymers such as glass laminate aluminum reinforced epoxy (GLARE) is increasing.

Definition and Classification

The design goal in composite production is to obtain more desirable combination of properties that could be achieved according to principle of combined action, where properties of two different materials are combined to create a better and expected combination of properties. A composite is a solid material, consisting of two or more constituents, of different physical and chemical properties that combine at the macroscopic level to form a new material with characteristics significantly different from the individual constituents, often with enhanced mechanical properties. As shown in Fig. 1 composite is multiphase material, usually with two phases - matrix as a continuous, soft, ductile, formable material and reinforcement as high strength, high stiffness, and low thermal expansion material. A clear distinction should be made between composites and alloys. In the

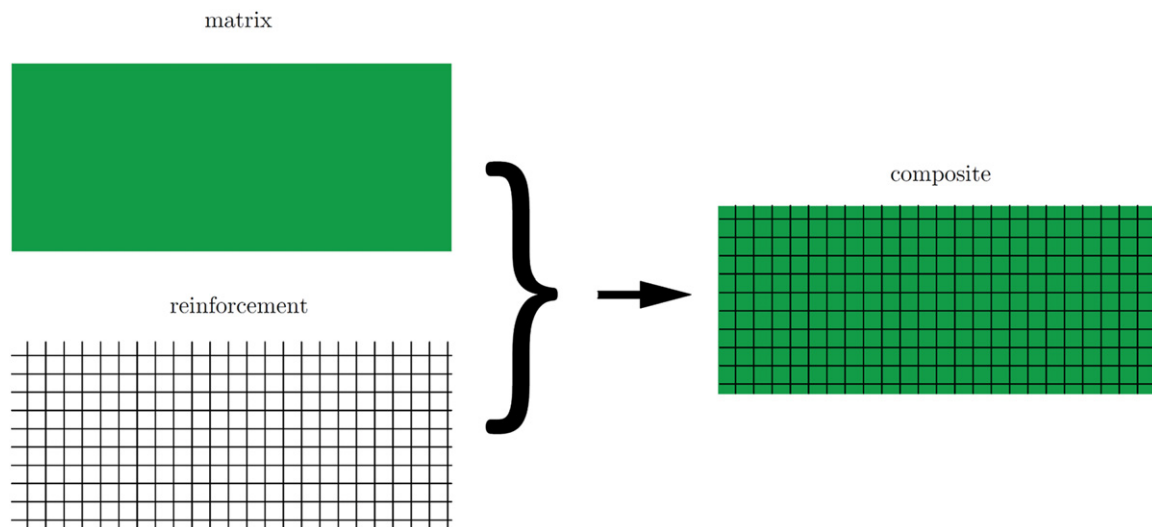


Fig. 1 Schematic representation composite.

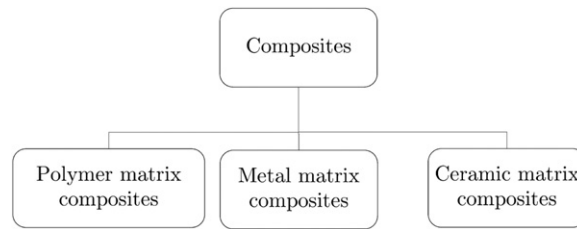


Fig. 2 Classification of composites – based on matrix materials.

composite as a final product, the individual components remain separated at the macroscopic level, while in the case of alloys, mixing takes place at the atomic level and leads to the production of completely new material.

Various authors suggest several ways of classifying composite materials (Jones, 1999), (Agarwal *et al.*, 2017), (Mallick, 1988), (Barbero, 2017). Fig. 2 shows the classification of composites based on matrix material as Polymer Matrix Composite (PMCs), Metal Matrix Composite (MMCs) and Ceramic Matrix Composite (CMCs).

There are 3 types of polymer matrix materials:

- thermoplastic
- thermoset
- elastomer

Thermoplastics are the most common among polymer matrices, providing good combination of strength and durability, but are extremely temperature and strain rate sensitive. Emergence of new biocompatible materials on the market, PLA (Murariu and Dubois, 2016) and PEEK (Kumar *et al.*, 2018) as matrix and carbon fibers as reinforcement with new additive technologies, such as 3D printing increased interest in industry and academics in recent years (Fu *et al.*, 2017). Thermosets are generally stronger than thermoplastic materials due to the 3D crosslinking, and are also better suited to high-temperature applications due to strong covalent bonds between polymer chains. Thermoset is irreversibly hardened by curing from viscous liquid prepolymer or resin and cannot be recycled. Most common thermoset composite examples are polyester (Gautier *et al.*, 1999) and epoxy-carbon (Guzmán *et al.*, 2014) composites. Elastomers as matrix are applied because of higher elongation and toughness (Millereau *et al.*, 2018), mainly used in steel reinforced tires (Rios *et al.*, 2001) or in carbon fiber reinforced polymers (CFRP) (Kizaki *et al.*, 2018).

MMCs are a group of materials (metals or intermetallic compounds) incorporated with various reinforcements, continuous fibres or particulates. Metal matrices are the most common in the industry, in composites that require higher strength, stiffness, elevated-temperature capabilities, high thermal conductivity and corrosion resistance (Haghshenas, 2016). Examples of most commonly used metallic matrix are composites based on:

- aluminum
- magnesium
- titanium
- copper
- super alloy

Ceramic matrices are brittle and have lower stiffness, which is improved by the addition of agents, in the same way as the strength of metal composites is improved by the addition of reinforcement. CMCs are composed of a ceramic matrix:

- SiC
- Al₂O₃
- SiN

and embedded metallic or ceramic fibers.

Fig. 3 shows the classification of composites based on reinforcement material into fiber reinforcement composites (FRCs) and particulate composites. The main difference between these two groups is the way of reinforcing. FRCs contain high-strength continuous or short reinforcing fibers while in particle composites aspect ratio of the reinforcement length to diameter is approximately equal to 1, usually sand size. Unlike high-strength reinforcing fibers, particles do not contribute to the load-carrying capacity of material and acts more like filler for the matrix and are predominantly used in CMCs and MMCs.

Fiber Reinforced Composites (FRC)

From an engineering point of view, FRCs represent the most common and technologically advanced composites, which are increasingly replacing metals, steel and aluminum alloys (Bakis *et al.*, 2002). FRCs consist of high-strength fibers embedded in a lower-strength matrix, with a clear interface between them. According to the definition of composite materials, fibers and matrix retain their physical and chemical properties in the composite, while in combination they give the material with superior properties compared to the constituents (Mallick, 1988). Fibers and matrices, in addition to retaining their properties, have

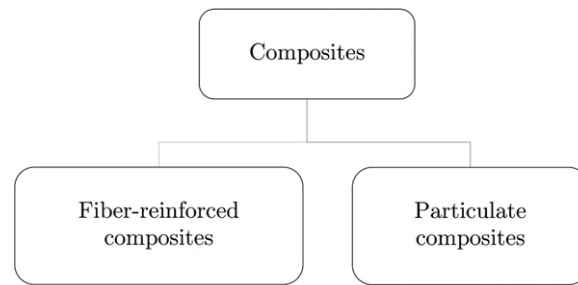


Fig. 3 Classification of composites – based on reinforcement.

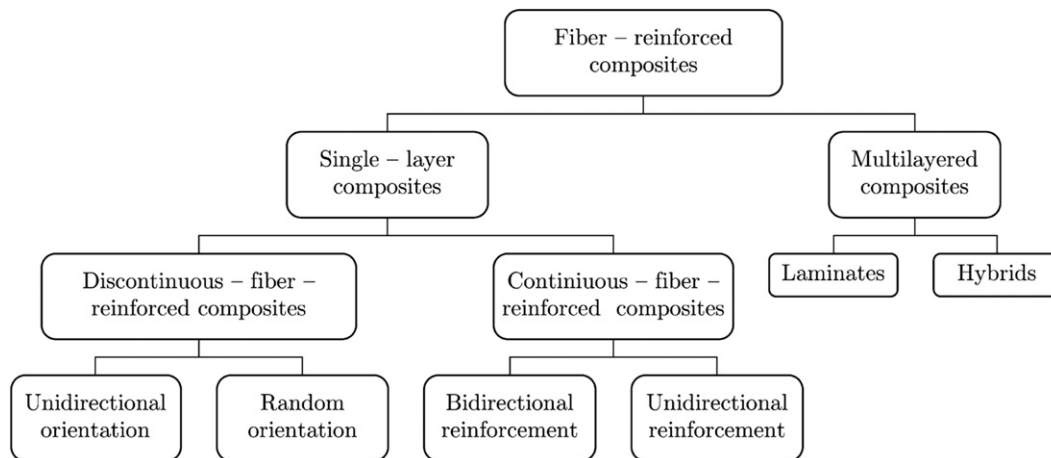


Fig. 4 Classification of FRC. Reproduced from Agarwal, B., Broutman, L., Chandrashekhara, K., 2017. Analysis and Performance of Fiber Composites. Wiley.

different roles in the composite material. Design of FRCs is flexible allowing reinforcement of certain zones, according to the application, in order to improve mechanical properties, such as compression and tensile stress, for the same or lower amount of mass. Because of their low density, the strength-weight ratios and modulus-weight ratios of these composite materials are usually superior to those of metallic materials, even in case of fatigue strength and failure damage. The group of FRC includes different combination of fibers and matrices, but due to the significantly increased use, primarily in industry, this term most often refers to fiber reinforced plastics (FRP). FRPs have emerged as a major class of structural materials and are either used or being considered for use in many weight-critical components in aerospace, automotive and other industries.

During the production of FRCs, a large number of fibers are embedded into a thin layer of matrix to form a single lamina or ply, the basic unit of composite structure. The thickness of the lamina is usually 0.1–1 mm in FRP, but may be significantly thicker, even 10 mm in MMCs. Single-layer composites are rare, except for special purposes in experiments or research. More often, multi-layer composites which can respond to the complex mechanical conditions are used. As shown in Fig. 4 FRCs are classified as single-layer and multilayer composites. According to the type of fibers, single-layer FRCs can be divided as:

- continuous (long) FRC
 - unidirectional reinforcement
 - bidirectional reinforcement
- discontinuous (short) FRC
 - unidirectional orientation
 - random orientation

Schematic representation of fiber orientation is given in Fig. 5. The main difference between continuous and discontinuous reinforcing fibers is the ratio between fiber length and diameter. For continuous fibers, which may be several meters long while the diameter is on a micro scale, this ratio is $10^4 \div 10^6$. Continuous fibers may be oriented either unidirectionally or bidirectionally. The discontinuous fibers can be arranged either in unidirectional orientation or in random orientation. For lamina containing unidirectional fibers, the composite material has highest strength and stiffness in the longitudinal direction of the fibers, while in transverse direction, its strength and stiffness are very low. For a lamina containing bidirectional fibers, the strength and modulus

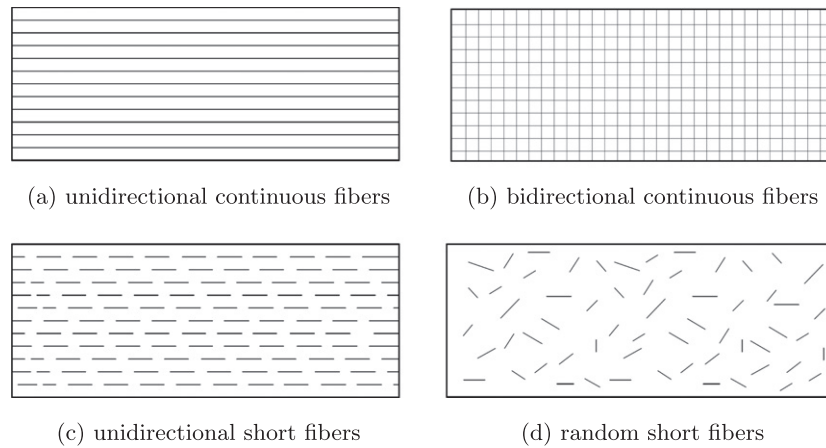


Fig. 5 Fiber orientation in single layer composites. (a) unidirectional continuous fibers. (b) bidirectional continuous fibers. (c) unidirectional short fibers. (d) random short fibers.

can be varied using different amounts of fibers in the longitudinal and transversally directions, while balanced lamina has same properties in both directions. As expected, discontinuous fiber-reinforced composites have lower strength and modulus comparing continuous fiber composites. Random oriented is better choice when direction of load is unknown or load can come from any direction.

Multilayer composites may be classified as:

- laminates
- hybrids

Laminates are made by stacking a large number of thin layers of lamina and consolidating them into desired thickness. Fiber orientation in each lamina, as well as stacking sequence of various laminae in a composite may controlled in order to obtain appropriate mechanical properties.

Hybrid composites are materials that consist of fibers embedded in a single matrix to form intraply hybrid laminate (Dhar Malingam *et al.*, 2018). Different FRP laminas can also be combined with metallic sheets to form metal-composite hybrids, commonly known as fiber metal laminates (FMLs). Two such commercial metal-composite hybrids are ARALL and GLARE, alternate layers of aluminium sheets and unidirectional aramid fiber-epoxy laminates and alternate layers of aluminium sheets and either unidirectional and bidirectional S-glass fiber epoxy laminates, respectively.

Fibers

Fibers determine the mechanical properties of the composite, providing stiffness, strength and reducing mass of material. Factors that govern the fibre's contribution are:

- the basic mechanical properties of the fibre itself
- the surface interaction of fibre and matrix (interface)
- the amount of fibre in the composite (fibre volume fraction)
- the orientation of the fibres in the composite

Reinforcing fibers have far greater tensile strength than bulk material from which they are made. The higher fiber strength lies in the structure of the material. Fibers are extremely long, with very small diameter, and there are almost no defects along the fiber, which makes them almost ideal material, resulting in much higher tensile strength compared to bulk material. For example, tensile strength of bulk E-glass is low, 1.5 GPa while in fiber form it may be 3.5 GPa. In Table 1 comparison between tensile strength of selected materials in form of fiber and bulk material is given.

Values for tensile strength of fibers are the mean value of a number of tests on individual fibers. Fiber strength is not unique and individual fibers strengths follow a Weibull distribution (Barbero, 2017). The cumulative probability of a fiber failing with strength less than or equal to σ is given by:

$$F(\sigma) = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad (1)$$

where σ_0 is the Weibull scale parameter and m is the Weibull shape parameter, related to the average strength. Values for metals and known composites are given in Table 2. Specific strength and specific stiffness are of importance, showing that with proper engineering composites provide same or higher stiffness and strength for lower mass. For example, carbon-epoxy has a lot higher specific stiffness and higher specific strength which is one of the reasons to be applied in airplanes (Mathijssen, 2018) and wind turbines (Steigmann *et al.*, 2016) where reducing of mass without reducing stiffness and strength is required.

Table 1 Comparison of tensile strength of fibers and bulk material

Material	Tensile strength (GPa) (fiber)	Tensile strength (GPa) (bulk)
Glass	3.5–4.6	0.7–2.1
Tungsten	4.2	1.1–4.1
Beryllium	1.3	0.7
Graphite	2.2–2.25	Very low

Table 2 Comparison of mechanical properties of solid materials and composites

Material	f (%)	E (GPa)	σ_u	ρ	Specific modulus	Specific strength
Steel	–	210	0.5–0.8	7.8	26.9	0.058–0.106
Aluminium	–	73	0.41	2.3	27	0.152
Glass-Epoxy	57	21.5	0.57	1.97	10.9	0.26
Kevlar-Epoxy	60	40	0.65	1.4	29	0.47
Carbon-Epoxy	58	83	0.38	1.54	53.5	0.24

Table 3 Properties of selected commercial reinforcing fibers

Fiber	Typical diameter	ρ	Tensile modulus	Tensile strength	Failure strain	Poisson's ratio
E-glass	10	2.54	72.4	3.45	4.8	0.2
S-glass	10	2.49	86.9	4.3	5.0	0.22
Kevlar-49	11.9	1.45	131	3.62	2.8	0.35
T-300	7	1.76	231	3.65	1.4	0.2
SiC	140	3.08	400	3.44	0.86	–

Tensile properties listed in [Table 3](#) are the average values reported by the fiber manufacturers. Stress-strain curves for given fibers are shown in [Fig. 6](#) obtained using the single filament test, designated as ASTM D3379, the tension test is carried at the constant loading rate until the filament fractures. Types of fibre reinforcement according to length – discontinuous(short) and continuous (long); stiffness – low(LM), medium(MM), high(HM) and ultra-high modulus(UHM); chemical composition – organic(poly-meric) and inorganic(glass, carbon, boron, ceramic, metallic).

Matrix

Performance of composite is strongly dependent of matrix material. Matrix material has various purposes in composite:

- holds fibers
- transfers the load through interface to the fibers
- transfers the load to the composite from external sources
- protect composite from the environment

Opposite of fibers, matrix properties influences transverse stiffness, transverse strength, shear strength and shear modulus. Since cross-sectional area of fiber is very small, it cannot be loaded directly. Also, fibers without matrix are mechanically isolated and cannot transfer load, specially in compression. Matrix material is used to bind fibers together in solid physical shape, and enables gripping and applying load and transfer load between different fibers which leads to a efficient structure. Beside mechanical properties, matrix determines maximum operating temperature of composite. Since matrices are dominantly plastics or polymers like epoxy, PEEK, polyester, that makes them light, flexible and weaker relatively to fibers. On the other hand, polymers are characterized by a glass transition temperature (T_g), at which polymers transition from solid to rubber phase. This means that even at temperatures close to T_g there is a sharp drop in the mechanical properties of the material, ([Slavkovic et al., 2017](#)) as a result of which it primarily leads to a weaker interface and load transfer and often faster failure of the composite. In addition to T_g , polymer matrices are characterized by visco-plastic behavior as well as strain rate dependence. Operating temperature ranges are given in [Fig. 7](#). Thermal stability of selected polymers is given in [Table 4](#).

Multi-Scale Mechanical Analysis of FRCs

In the structural analysis of composite materials, main goal is to understand the mechanical behaviour under external loads and constraints. Multiple scales are used for mechanical analysis of composites, i.e., mechanical behaviour of laminate, lamina and

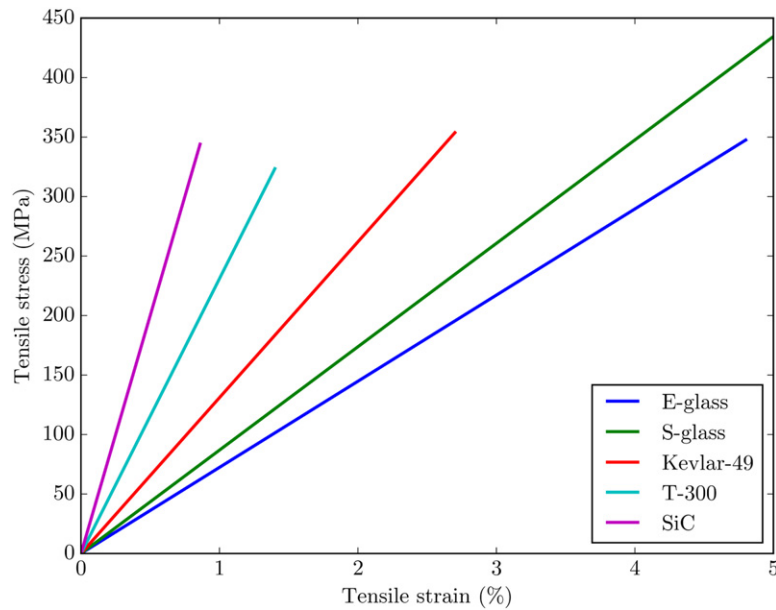


Fig. 6 Tensile stress-strain diagrams for various reinforcing fibers.

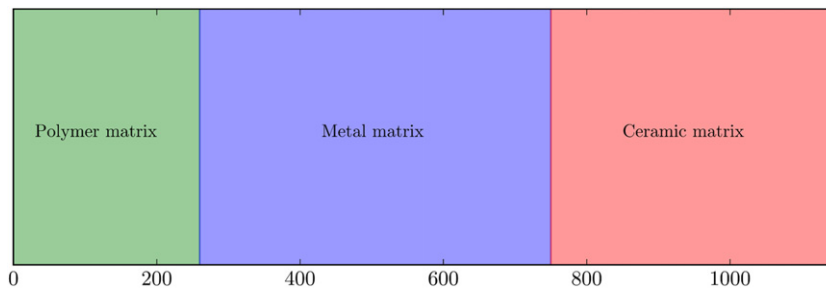


Fig. 7 Temperature range of matrix materials.

Table 4 Thermal stability of selected matrix polymers

Polymer	Glass Transition Temp. T_g	Max. use temp. $^{\circ}\text{C}$
PLA	55–65	45
Polyester	80–100	50
Epoxy	120–180	150
PEEK	143	250
Polycarbonate	145	125

micromechanical behaviour of constituents are considered, as shown in Figs. 8 and 9. Analysis of each of the scales requires different methods and techniques (Jones, 1999; Bohm, 2004). Micromechanical scale analysis deals with the behaviour of composites at the level of constituents – fibers and matrix. This allows the heterogeneous material to be represented by effective elastic properties for the homogenized material. Using the effective properties obtained at the lowest level of mechanical analysis, it is possible to define a theory of the mechanical behaviour of a laminate structure Classical Laminate Theory (CLT), which is part of macromechanics. CLT defines the behavior of composite at lamina level based on the effective properties of composite material obtained from micro-mechanical models. It may include finite element analysis (FEA) of composite structure using homogeneous effective properties determined using micro-mechanical analysis. The results obtained using CLT are used in the structural mechanical analysis of composites to define the overall behavior of the structure. Thus, the most general approach is to use micro-mechanical results integrated with macro-mechanical with structural mechanics can be used in the analysis of advanced composite structures in order to understand the behavior of 3D composite structure on the highest scale.

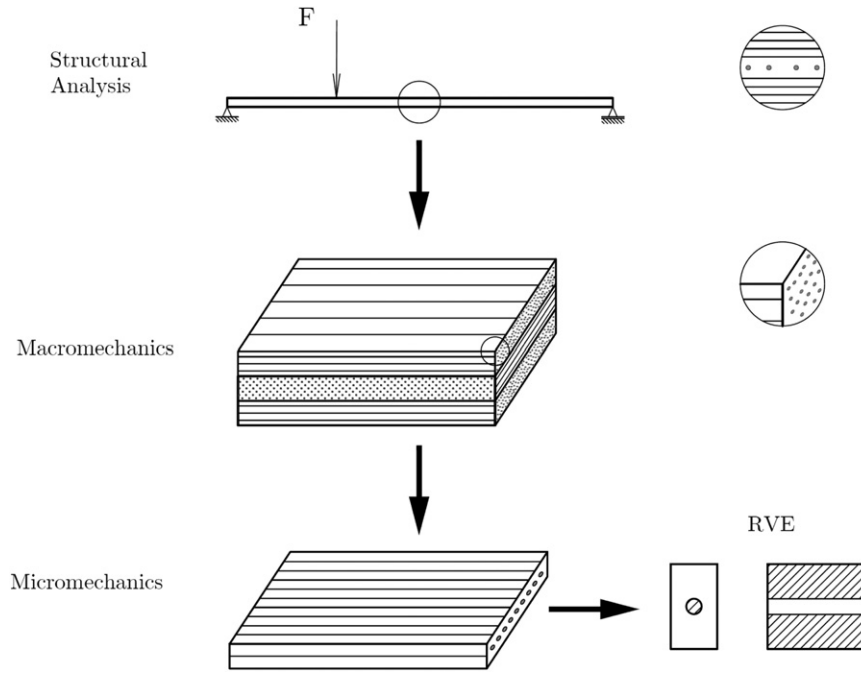


Fig. 8 Different length scales.

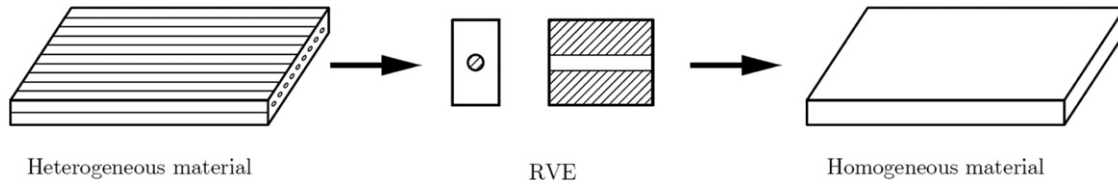


Fig. 9 Micromechanical homogenization of composite material.

Micromechanics

Micromechanics is the analysis of composite or heterogeneous materials on the level of the individual constituents - fibers and matrix. Micromechanics also deals with the influence of its fiber volume fraction on the composite behaviour and the detailed examination of interface behaviour between the fibre and matrix (Jones, 1999). Micromechanics is used to determine stiffness (very successful) and strength (less successful) (Barbero, 2017). Micromechanical analysis is an important and most common approach to assess the effective elastic constants of composite materials from known mechanical properties of their individual constituent materials through Representative Volume Element (RVE) model of composite. The key point of micromechanics of materials is the localization, which aims at evaluating the local fields of stress and strain in the phases for given macroscopic load states, phase properties, and phase geometries, which is very useful in damage and failure analysis.

The behavior of composite materials is significantly influenced by the relative amount of each of the constituents as well as the geometry of the part.

The main advantage of micromechanics is to perform virtual testing in order to reduce the cost of an experimental campaign. Indeed, an experimental campaign of heterogeneous material is often expensive and involve a larger number of permutations: constituent material combinations; fiber and particle volume fractions; fiber and particle arrangements; and processing histories. Once the constituents properties are known, all these permutations can be simulated through virtual testing using micromechanics.

Basic Concepts

Total mass of composite:

$$m_c = m_f + m_m \quad (2)$$

where m_c , m_f and m_m are mass fraction of composite, fibers and matrix, respectively. Dividing both sides with m_c :

$$1 = M_f + M_m \quad (3)$$

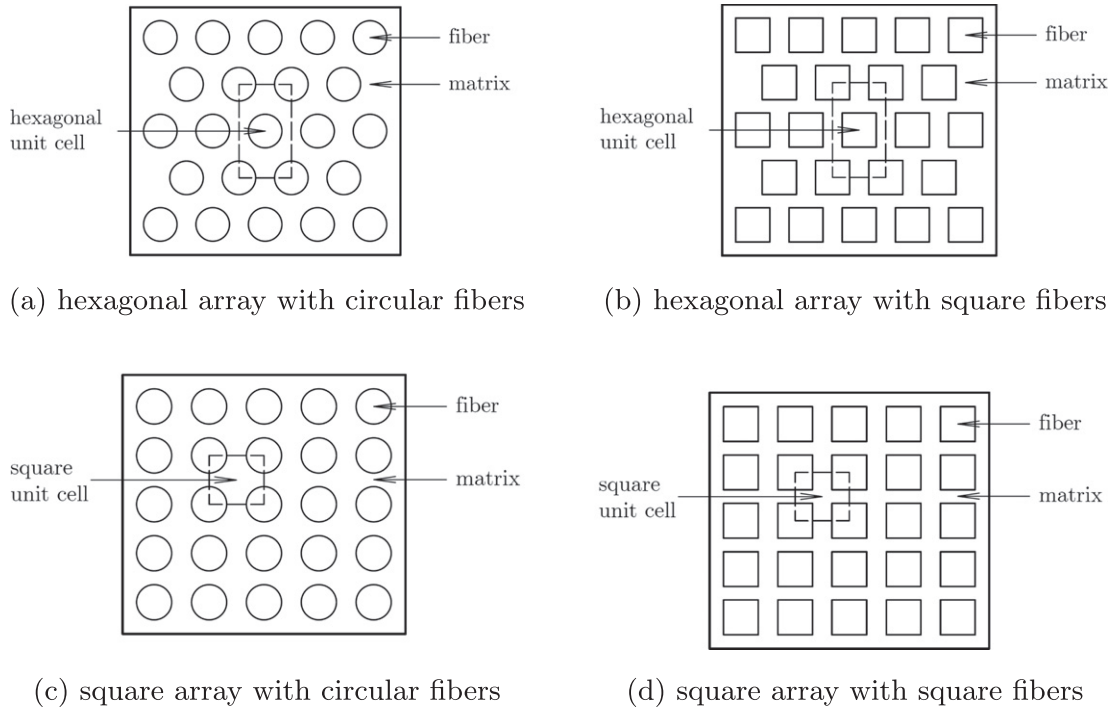


Fig. 10 Arrangement of fibers. (a) hexagonal array with circular fibers. (b) hexagonal array with square fibers. (c) square array with circular fibers. (d) square array with square fibers.

where M_f is mass fraction for fiber, and M_m is mass fraction of matrix. Total volume is the sum of the fiber and matrix volume:

$$1 = V_f + V_m \quad (4)$$

For ease of notation all the equations are given in terms of fiber volume fraction with $V_f = f$ and, consequently, $V_m = 1 - f$.

The arrangement of fibers in the composite is quite irregular, more statistical than deterministic, but it is possible to isolate periodic arrangement of fibers. Micromechanical analysis is based on the selection of a sub-volume called representative volume element (RVE). RVE should be of sufficient size to provide accurate geometry that includes both constituents, and to have the same elastic constants and fiber volume fractions as the composite. Subsequently, the behaviour of RVE may be considered as the basis for macrolevel analysis by taking the effective mechanical properties obtained using homogenization process (Nemat-Nasser *et al.*, 1996). Common unit cells are square and hexagonal shape with assumption that cross section of fibers is either square or circular (Devireddy *et al.*, 2014). For square RVE the fiber volume fraction is calculated by:

$$f = \frac{a_1(\pi/4)d_f^2}{a_1a_2a_3} \quad (5)$$

where f is fiber volume fraction; a_1, a_2, a_3 are the length of square RVE; and d_f is the diameter of fiber. Hexagonal packing geometry allows more compact design of composite than square packing geometry. For hexagonal RVE the fiber volume fraction is calculated by:

$$f = \frac{2a_1(\pi/4)d_f^2}{a_1a_2a_3} \quad (6)$$

where $a_3 = a_2 \tan 60^\circ$ and $a_2 = 4a_1$. The case can be simplified as planar if we consider that the depth a_1 is the same for the fiber and the matrix, i.e., the interface is complete. For a square and hexagonal packing RVE shown in Fig. 10 the maximum theoretically achievable fiber volume fractions are 0.7854 and 0.9069 (Taranu *et al.*, 2012) respectively.

Micromechanical Modelling of Stiffness

Unidirectional fiber reinforced composites

There are several groups of micromechanical models used to characterize the elastic behaviour of FRCs: strength of materials (SOM), semi-empirical, elasticity and numerical models. In order to evaluate the elastic stiffness of the unidirectional lamina, the following assumptions are made (Agarwal *et al.*, 2017):

- perfect bond between matrix and fibre
- fibres are continuous and parallel

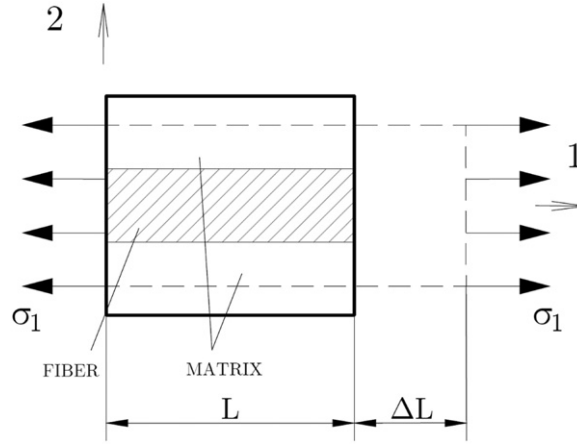


Fig. 11 Representation of Voigt model.

- the fibres are uniformly distributed in the matrix
- linear elastic law (Hook's law) applied on fibres and matrix
- no voids in composite
- elastic moduli, diameters, space between fibres are uniform

ROM models are simple analytical models that give a sufficiently accurate prediction of the elastic constants of composites. Starting from the general formula for ROM of scalar effective values of physical properties for two phase composite (Bohm, 2004):

$$\psi = \left[f(\psi_r)^k + (1-f)(\psi_m)^k \right]^{\frac{1}{k}} \quad (7)$$

where r and m denote, reinforcements (fibers or particles) and matrix, respectively, f is fiber volume fraction, while the exponent k can be fitted according to experimental data. Changing $k = 1$ and $k = -1$ in Eq. (7) gives Voigt (Voigt, 1887) and Reuss model (Reuss, 1929), respectively. Main assumptions made in ROM models are good constituent connections, similar Poisson's coefficient and ignoring time-dependent matrix behavior.

Voigt analytical solution for ROM is the simplest model for determining the stiffness of FRCs composites when the load is applied along direction parallel with fibers. Crucial assumption is that strain is equal in composite, fibres and matrix $\varepsilon_1 = \frac{\Delta L}{L}$ as shown in Fig. 11:

$$\varepsilon_1 = \varepsilon_m = \varepsilon_f \quad (8)$$

Load is applied along the direction parallel with fibres and the stress is used for quantification:

$$\sigma_1 A = \sigma_m A_m + \sigma_f A_f \quad (9)$$

and with Hook's law:

$$\varepsilon_1 E_1 A = \varepsilon_m E_m A_m + \varepsilon_f E_f A_f \quad (10)$$

Dividing both sides with A_c and ε_c :

$$E_1 = E_f \frac{A_m}{A} + E_m \frac{A_f}{A} \quad (11)$$

Longitudinal stiffness of composite is given by:

$$E_1 = f E_f + (1-f) E_m \quad (12)$$

where subscripts f and m denotes fibres and matrix, respectively. Eq. (12) is known as the ROM expression for stiffness.

Equation for E_1 may be normalized with E_m :

$$\frac{E_1}{E_m} = f \frac{E_f}{E_m} + (1-f) \quad (13)$$

$$\frac{E_1}{E_m} = f \left(\frac{E_f}{E_m} - 1 \right) + 1 \quad (14)$$

This two equations give a good perspective of significant influence of E_f on the overall E_1 .

If we consider two types of fibers, glass and graphite fibers:

$$\frac{E_f}{E_m} \approx 20 \quad (15)$$

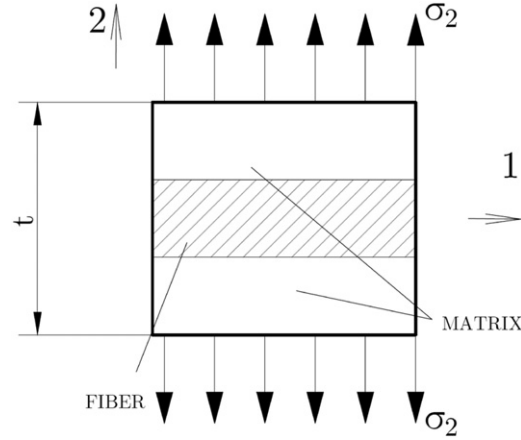


Fig. 12 Representation of Reuss model.

$$\frac{E_f}{E_m} \approx 100 \quad (16)$$

Computing E_1/E_m for $f = 10\%$ and $f = 50\%$ for both fibers shows that even small amount of glass fibers increases modulus by almost three times and for highly stiff graphite fibers, small amount of fibers significantly increases stiffness of composite, even 10 times. Also, with increasing amount of fibers specific stiffness which is ratio of moduli and density changes significantly especially in case of light and extremely stiff graphite fibers.

Reuss model is a simple micromechanical model for determining the transverse stiffness of FRCs. Reuss type of ROM is based on assumption that matrix and fibres of composite are subjected to the same stress:

$$\sigma_2 = \sigma_m = \sigma_f \quad (17)$$

Total thickness is:

$$t = t_m + t_f \Rightarrow \Delta t = \Delta t_f + \Delta t_m \quad (18)$$

and strain relation $\varepsilon = \frac{\Delta t}{t}$ we get **Fig. 12**:

$$\varepsilon_2 t = \varepsilon_f t_f + \varepsilon_m t_m \quad (19)$$

$$\varepsilon_2 = \varepsilon_f \frac{t_f}{t} + \varepsilon_m \frac{t_m}{t} \quad (20)$$

Using Hook's law and equality of stress:

$$\frac{\sigma_2}{E_2} = (1-f) \frac{\sigma_m}{E_m} + f \frac{\sigma_f}{E_f} \quad (21)$$

Finally:

$$\frac{1}{E_2} = \frac{f}{E_f} + \frac{1-f}{E_m} \quad (22)$$

Normalized E_2 is given with:

$$\frac{E_2}{E_m} = \frac{E_f}{f + (1-f)E_f/E_m} \quad (23)$$

Fig. 13 shows that value of the E_2 increases twice as much as the matrix modulus E_m in region where fiber volume fraction is 50%–60%, which is common for most FRPs given in **Table 2**. Using the Eq. (23), it is concluded that the fibers significantly affect the value of E_2 only for a large, theoretical values of f given with Eqs. (5) and (6), even when fibers are significantly stronger than the matrix.

The Reuss model may be modified to include Poisson's effect in matrix material by introducing a constrained matrix modulus, effectively by dividing E_m by $(1 - \nu_m^2)$:

$$\frac{1}{E_2} = \frac{f}{E_f} + \frac{(1-f)(1 - \nu_m^2)}{E_m} \quad (24)$$

This correction has a small overall effect on the total value of the transverse modulus and is less frequently taken into account in the analysis.

As in most cases the fibers are far stronger than the matrix, for practical application, ROM models can sufficiently enough approximated with:

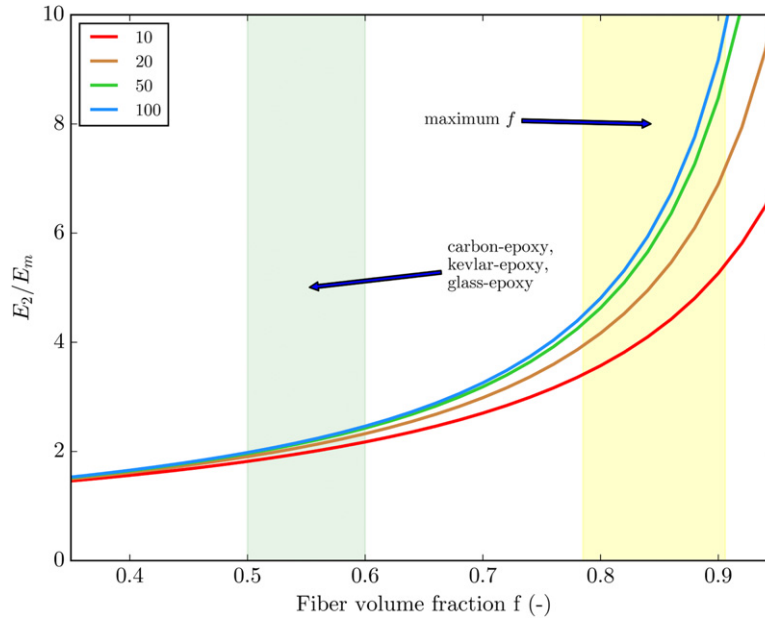


Fig. 13 Variation of normalized E_1 with fiber volume fraction f .

$$E_1 \approx fE_f \quad (25)$$

$$E_2 \approx \frac{1-f}{E_m} \quad (26)$$

It is clear from the above equations that the stiffness in the direction of the fibers is predominantly determined by the fiber modulus, while the transverse stiffness is determined by the modulus of the matrix.

Major Poisson ratio gives relation to the lateral strain when load is applied longitudinally:

$$v_{12} = -\frac{\varepsilon_2}{\varepsilon_1} \quad (27)$$

Analogous to Voigt ROM:

$$v_{12} = (1-f)v_m + fv_f \quad (28)$$

Eq. (28) is known as ROM for the Poisson's ratio. Minor Poisson ratio relation with v_{12} is given by Fig. 14:

$$\frac{v_{21}}{E_2} = \frac{v_{12}}{E_1} \quad (29)$$

Finally:

$$v_{21} = v_{12} \frac{E_2}{E_1} \quad (30)$$

Although values of Poisson ratio are rarely significantly different, because of $E_1 \gg E_2$ it should be mentioned that $v_{21} \neq v_{12}$. As shown in Fig. 15, when composite with fiber is loaded by an in-plane shear stress. With assumption that fibers and matrix carry same stress:

$$\frac{1}{G_{12}} = \frac{f}{G_f} + \frac{(1-f)}{G_m} \quad (31)$$

Normalized G_{12} is given with:

$$\frac{G_{12}}{G_m} = \frac{G_f}{f + (1-f)G_f/G_m} \quad (32)$$

As in the case of E_2 , the modulus of the matrix is the dominant term in the formula for G_{12} . Only when the fiber volume fraction is greater than 50% of the total volume does the G_{12} value doubles, even if the matrix is 100 times stronger than the fiber.

ROM models are boundary curves for E_1 and E_2 values. Actual experimental values often lie between these two curves as given in Figs. 16 and 17 for boron-epoxy composite. The experimental values of E_1 most often show a good match with the Voigt model, while the experimental values of E_2 are higher than the Reuss model. The reasons for these difference lie in the initial assumptions of model. It may be concluded:

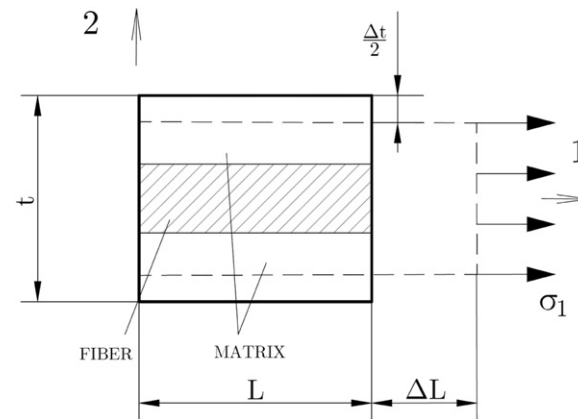


Fig. 14 Poisson ratio calculation.

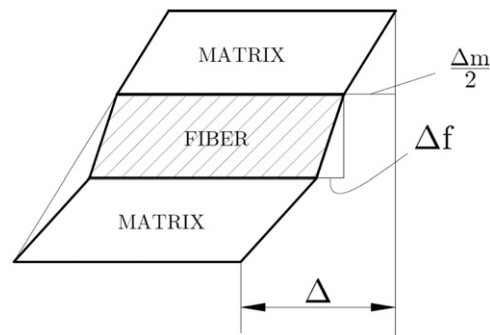


Fig. 15 Representation of Reuss model.

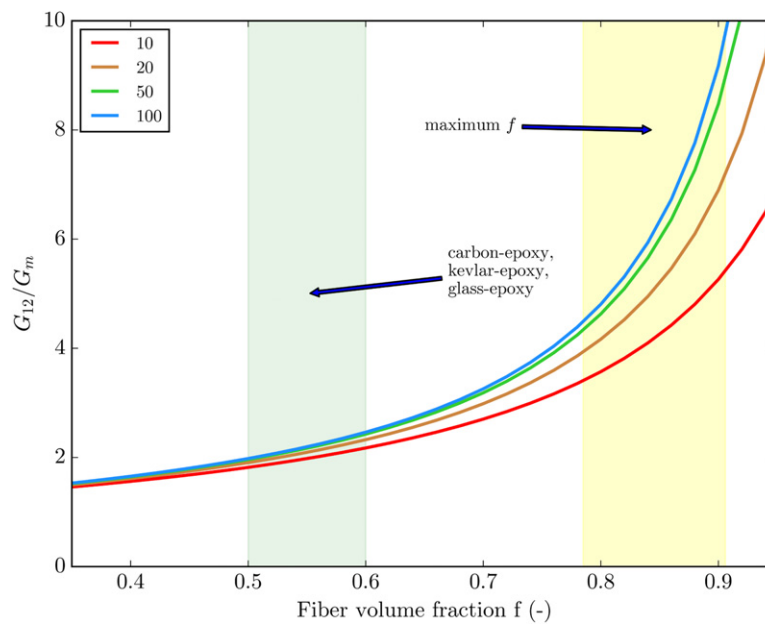


Fig. 16 Variation of normalized G_{12} with volume fraction f .

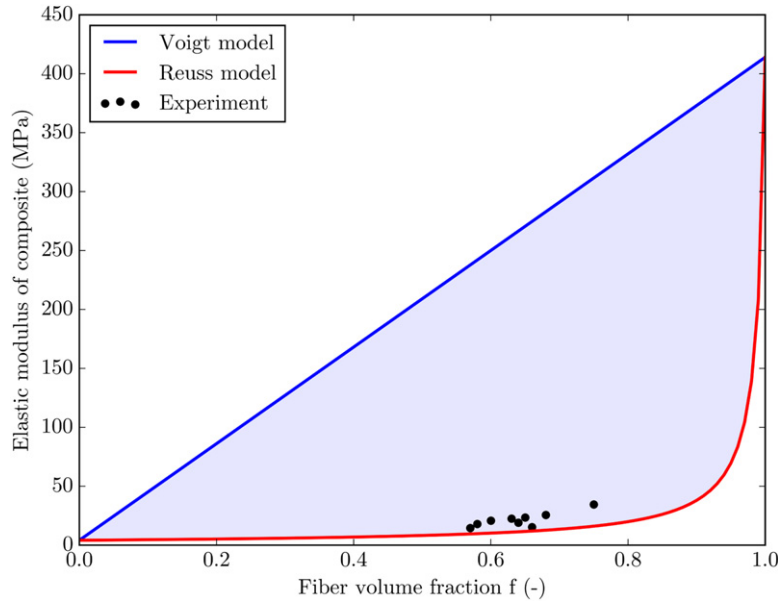


Fig. 17 ROM curves. Reproduced from Hashin, Z., 1970. Nasa tech. rep. contract no. nasi-8818.

- fibers are continuously dispersed in the medium in transverse direction, load is shared between fiber and matrix so $\sigma_f = \sigma_c = \sigma_m$ is not valid assumption
- Poisson's contraction due to transverse load is not same in fiber and matrix. Fibers constrain expansion of the matrix, which leads to smaller value of δ_c , and greater value for E_2 Eq. (14).

ROM models, in addition to certain inaccuracies, are considered the most efficient models that provide effective elastic properties with sufficient accuracy and high computer efficiency, since for designing and modeling composites, it is more important to have simpler and more computer-efficient models for approximating elastic constants.

Although efficient, ROM models often give inaccurate approximations, especially for transverse properties. Empirical models represent a compromise between simple elastic models and series of realistic models that involve fiber distribution and give results similar to experimental ones. Halpin and Tsai (Tsai, 1970) developed a semi-empirical model to evaluate the elastic constants of composites accurately. The given model represents a mathematical, best-known semi-empirical model that gives a reasonable prediction of the transverse stiffness. The model provides relations for transverse moduli and shear modules:

$$E_2 = E_m \frac{1 + f\zeta\eta_E}{1 - f\eta_E} \quad (33)$$

$$G_{12} = G_m \frac{1 + f\zeta\eta_G}{1 - f\eta_G} \quad (34)$$

with parameter η given in the form of ratio of relevant fiber matrix modules E_f/E_m and G_f/G_m while ζ is a reinforcing factor depending on the loading direction:

$$\eta_E = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta} \quad (35)$$

$$\eta_G = \frac{\frac{G_f}{G_m} - 1}{\frac{G_f}{G_m} + \zeta} \quad (36)$$

The parameter ζ is a reinforcing factor related to the geometry of the fibers and the packaging arrangement of the fibres:

- circular cross section of $\zeta = 2$
- rectangular cross section $\zeta = 2 \frac{a}{b}$

It may be concluded that:

- transverse modulus changes marginally with increasing E_f/E_m
- transverse modulus changes moderately with f
- longitudinal modulus is sensitive to changes of f and E_f/E_m

Transverse elastic modulus and shear strain with Chamis model (Chamis, 1989) are given with:

$$E_2 = \frac{E_m}{1 - \sqrt{f}(1 - \frac{E_m}{E_f})} \quad (37)$$

$$G_{12} = \frac{G_m}{1 - \sqrt{f}(1 - \frac{G_m}{G_f})} \quad (38)$$

Nielsen model (Krishnamachari and Broutman, 1993) is reformulated Halpin-Tsai model, in order to include the influence of the maximum fiber packaging fraction $f_{\max}$:

$$E_2 = E_m \frac{1 + f\zeta\eta_E}{1 - f\psi\eta_E} \quad (39)$$

$$G_{12} = G_m \frac{1 + f\zeta\eta_G}{1 - f\psi\eta_G} \quad (40)$$

with:

$$\eta_E = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta} \quad (41)$$

$$\eta_G = \frac{\frac{G_f}{G_m} - 1}{\frac{G_f}{G_m} + \zeta} \quad (42)$$

and:

$$\psi = 1 + \frac{(1 - \psi_{\max})}{\psi_{\max}^2} f \quad (43)$$

where:

- for a square array fibers $\psi_{\max} = 0.785$
- for a hexagonal arrangement fibers $\psi_{\max} = 0.905$

Mori-Tanaka (Tucker III and Liang, 1999) method provides analytical solution based on Eshelby solution. The stress concentration tensor $\mathbf{B}^e$ which relates the strain of fibres to strain of matrix is given with:

$$\mathbf{B}^e = \mathbf{H}^e(\mathbf{I}, E_m, E_f) = \{\mathbf{I} + \zeta(\mathbf{I}, E_m) : E_m^{-1} : [E_f - E_m]\}^{-1} \quad (44)$$

where $\zeta(\mathbf{I}, E_m)$ is the Eshelby's tensor. Weakness of this model is less accuracy with rise of f .

The elasticity approach is based on a model called composite cylinder assemblage (CCA) model defined by Hashin and Rosen (1964). Model is shown in Fig. 18. The composite is considered to be made of repeating cylindrical RVEs, with cylindrical, continuous fibres are considered distributed in a periodic arrangement (Jones, 1999). The volume fraction of fibre is given with:

$$f = d^2 / D^2 \quad (45)$$

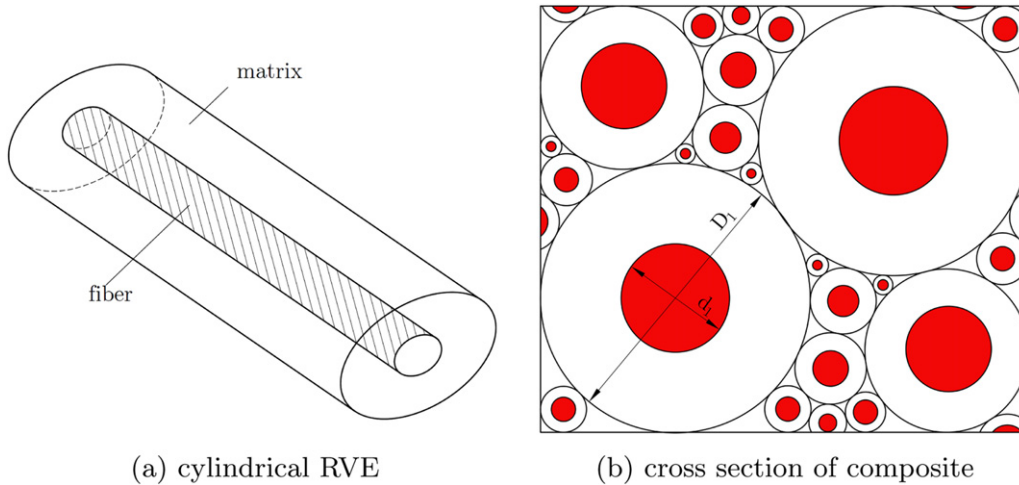


Fig. 18 CCA model. (a) cylindrical RVE. (b) cross section of composite.

Total volume is progressively filled with composite cylinders of different diameters. As the choice of cylinder diameter is arbitrary small, the remaining volume is consequently extremely small. During longitudinal loading, each of the composite cylinders behaves as an equivalent homogeneous cylinder. For uniform axial load, radial deformation in the transverse plane, as well as uniform axial shearing displacements and tractions gives the formulation of CCA model:

$$E_1 = fE_f + (1-f)E_m + \frac{4f(1-f)(v_f - v_m)^2}{\frac{1-f}{K_f} + \frac{f}{K_m} + \frac{1}{G_m}} \quad (46)$$

$$v_{12} = fv_f + (1-f)v_m + \frac{f(1-f)(v_f - v_m)\left(\frac{1}{K_m} - \frac{1}{K_f}\right)}{\frac{1-f}{K_f} + \frac{f}{K_m} + \frac{1}{G_m}} \quad (47)$$

$$K = K_m + \frac{f}{\frac{1}{K_f - K_m} + \frac{(1-f)}{K_m + G_m}} \quad (48)$$

$$G = G_m + \frac{f}{\frac{1}{G_f - G_m} + \frac{1-f}{2G_m}} \quad (49)$$

Using the presented models, analytical and experimental values for various cases of composites were compared. Analytical results of the models were obtained in the Python scripting language.

In Fig. 19 comparison of longitudinal modulus E_1 for carbon-epoxy (Kriz and Stinchcomb, 1979) ($E_f = 232$ GPa, $E_m = 5.35$ GPa, $v_f = 0.279$, $v_m = 0.354$) with analytical results is given. The results shows good agreement of Voigt model with experiment and significant influence of aspect ratio of the fiber for Mori-Tanaka model.

In Figs. 20 and 21 comparison of transverse modulus E_2 and shear modulus G_{12} for glass-epoxy (Tsai, 1964) ($E_f = 73.1$ GPa, $E_m = 3.45$ GPa, $G_f = 30.2$ GPa, $G_m = 1.8$ GPa, $v_f = 0.22$, $v_m = 0.35$) with analytical results is given. As expected, Reuss, Reuss modified and CCA give values significantly lower than experimental. On the other hand, semi-empirical models Chamis and Halpin-Tsai show good agreement with the experiment.

In addition to the above models and approaches, there are several others that are described in books (Jones, 1999; Agarwal et al., 2017) and papers (Heidari-Rarani et al., 2018).

Discontinuous fiber reinforced composites - preferred orientation

Longitudinal modulus:

$$E_1 = \frac{1 + 2(l_f/d_f)f\eta_1}{1 - f\eta_1} E_m \quad (50)$$

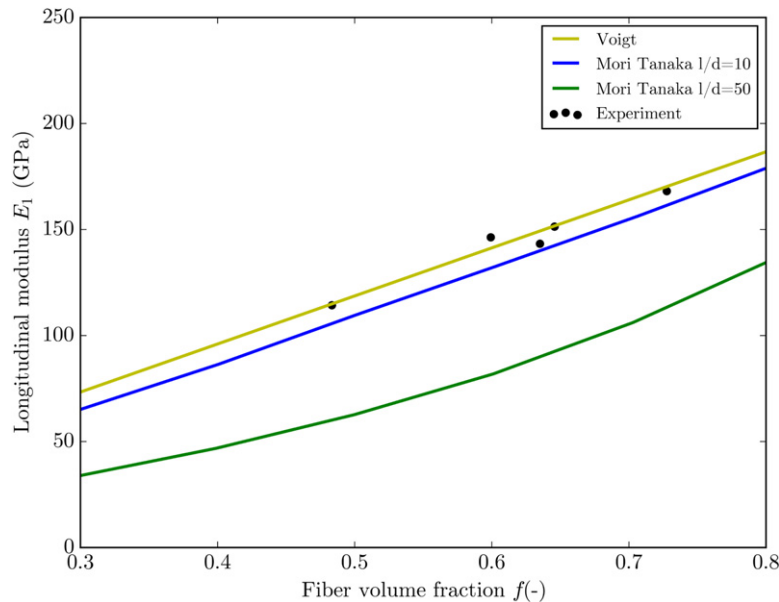


Fig. 19 Comparison of analytical and theoretical values of E_1 of carbon/epoxy as function of f fraction. Reproduced from Kriz, R.D., Stinchcomb, W.W., 1979. Elastic moduli of transversely isotropic graphite fibers and their composites. *Experimental Mechanics* 19, 41–49.

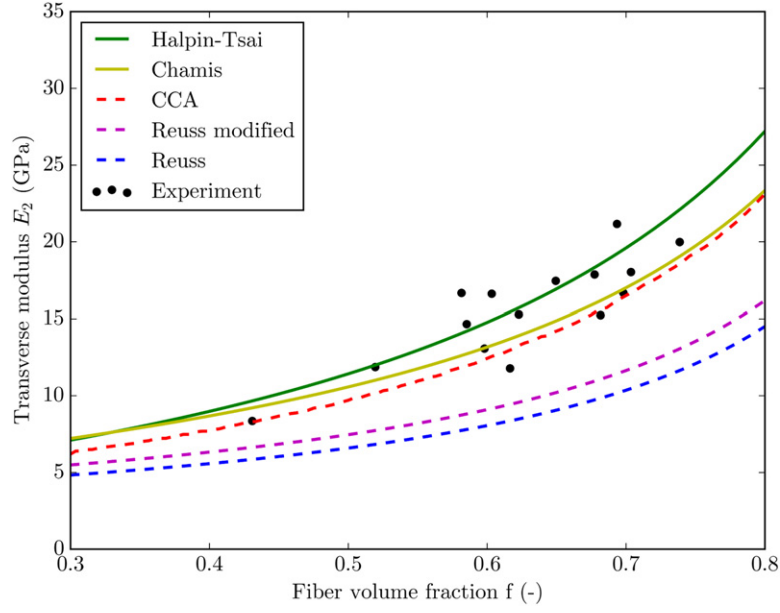


Fig. 20 Comparison of analytical and theoretical values of E_2 of glass/epoxy as function of f fraction. Reproduced from Tsai, S., 1964. Structural behavior of composite materials. Philco Corp Newport Beach Ca Space and Re-Entry Systems.

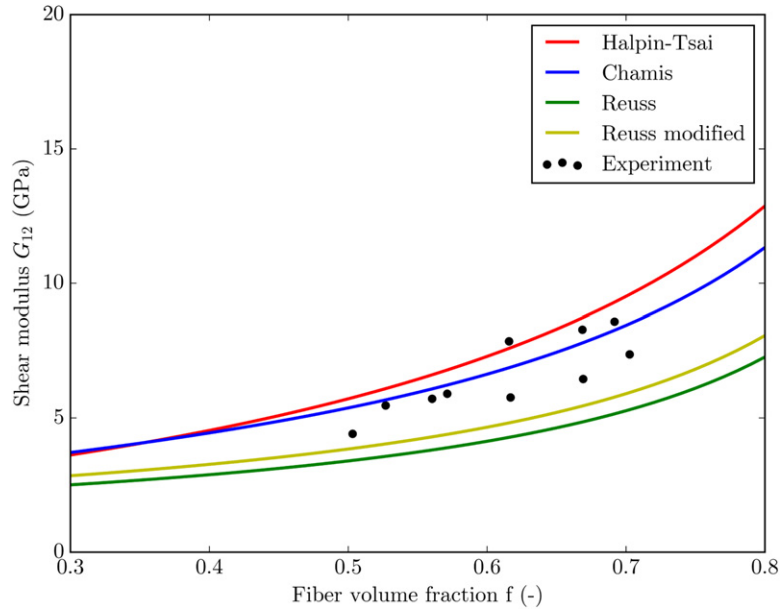


Fig. 21 Comparison of experimental and theoretical values of E_1 of carbon/epoxy in terms of fiber volume fraction. Reproduced from Noyes, J.V., Jones, B.H., 1968. Analytical Design Procedures for the Strength and Elastic Properties of Multilayer Fibrous Composites. American Institute of Aeronautics and Astronautics.

Transverse modulus:

$$E_2 = \frac{1 + 2f\eta_2}{1 - f\eta_2} E_m \quad (51)$$

Shear modulus:

$$G_{12} = G_{21} = \frac{1 + f\eta_{12}}{1 - f\eta_{12}} G_m \quad (52)$$

where:

$$\eta_1 = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l_f/d_f)} \quad (53)$$

$$\eta_2 = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2} \quad (54)$$

$$\eta_{12} = \frac{(G_f/G_m) - 1}{(G_f/G_m) + 1} \quad (55)$$

l_f and d_f in equations above are average fiber length and diameter of fibers in composite. Major and minor Poisson's ratio may be calculated using Eqs. (28) and (30). It should be noted that Eqs. (50)–(52) are special cases of Halpin-Tsai model for discontinuous FRCs, showing that E_1 is significantly influenced by length to diameter aspect ratio. Few assumptions are made:

- cross section of fiber is circular
- fibers are arranged in square unit cell
- fibers are uniformly distributed throughout the matrix
- perfect bonding between matrix and fibers
- no voids in matrix

As expected, longitudinal modulus E_1 of discontinuous FRC is lower than that for continuous one.

Discontinuous fiber reinforced composites – Random orientation

Composite with discontinuous randomly oriented fibers may be treated as isotropic planar case, with properties same in all directions in the plane. Tensile modulus:

$$E_r = \frac{3}{8}E_1 + \frac{5}{8}E_2 \quad (56)$$

Shear modulus:

$$G_r = \frac{1}{8}E_1 + \frac{1}{4}E_2 \quad (57)$$

where E_1 and E_2 are calculated using Eqs. (50) and (51), with given fiber aspect ratio and f . Poisson's ratio is:

$$\nu_r = \frac{E_r}{2G_r} - 1 \quad (58)$$

Mechanics of Lamina

Classical engineering materials such as ceramics, metals or polymers are usually considered isotropic, i.e. their properties do not change with the respect of direction. During making of composite, the two constituents can be homogeneous and isotropic, for example carbon fiber and epoxy matrix, while the composite itself can have anisotropic properties.

Fig. 22 shows a lamina with an arbitrary orientation of the fibers. We define two coordinate systems for lamina analysis. The axes in the 1–2 coordinate system are called the material axes or the local axes, where direction 1 is parallel to the fibers (also called the longitudinal direction) and direction 2 is perpendicular to the fibers (also called the transverse direction). The axes in the x-y coordinate system are called the global axes.

Angle θ , between the positive x-axis and 1-axis defines fiber orientation angle. In special cases, a 0° and a 90° lamina the material axis 1 coincides with the loading axis x, and the material axis 1 is at a 90° angle with the loading axis x, respectively.

Fiber-reinforced composites are generally considered to be orthotropic materials, i.e., have three planes of material symmetry, namely, 1–2, 2–3 and 1–3 planes according to the coordinate system in Fig. 22. In addition to orthotropy, two terms related to FRC are also defined:

- specially orthotropic material when the reference system of coordinates is selected along principal planes of material symmetry.
- transversely isotropic material – one of its principal planes is a plane of isotropy (properties are the same in all directions).

Stress and Strain Transformation in Thin Lamina Under Plane Stress

In stress analysis of a thin lamina with fiber orientation angle θ , the stresses in the global and material axes are related to each other through relations:

$$\sigma_{11} = \sigma_{xx}\cos^2\theta + \sigma_{yy}\sin^2\theta + 2\tau_{xy}\cos\theta\sin\theta \quad (59)$$

$$\sigma_{22} = \sigma_{xx}\sin^2\theta + \sigma_{yy}\cos^2\theta - 2\tau_{xy}\cos\theta\sin\theta \quad (60)$$

$$\tau_{12} = (-\sigma_{xx} + \sigma_{yy})\cos\theta\sin\theta + \tau_{xy}(\cos^2\theta - \sin^2\theta) \quad (61)$$

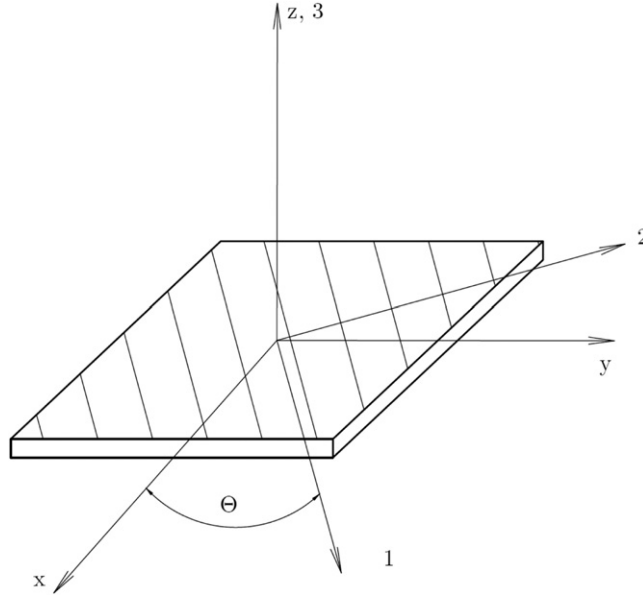


Fig. 22 Coordinate systems of thin arbitrary oriented lamina.

where σ_{xx} , σ_{yy} and τ_{xy} are applied stresses in the xy directions and σ_{11} , σ_{22} and τ_{12} are transformed stresses in the 12 directions.

$$\begin{Bmatrix} \sigma_{11} \\ \sigma_{22} \\ \tau_{12} \end{Bmatrix} = \begin{Bmatrix} \cos^2\theta & \sin^2\theta & 2\cos\theta\sin\theta \\ \sin^2\theta & \cos^2\theta & -2\cos\theta\sin\theta \\ -\cos\theta\sin\theta & \cos\theta\sin\theta & \cos^2\theta - \sin^2\theta \end{Bmatrix} \begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{Bmatrix} = \{T\} \begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{Bmatrix} \quad (62)$$

Similar equations can also be written for strain transformation by replacing each σ with ε and each τ with $\frac{1}{2}\gamma$ in previous equation. Thus, the strain transformation equations are:

$$\varepsilon_{11} = \varepsilon_{xx}\cos^2\theta + \varepsilon_{yy}\sin^2\theta + \gamma_{xy}\cos\theta\sin\theta \quad (63)$$

$$\varepsilon_{22} = \varepsilon_{xx}\sin^2\theta + \varepsilon_{yy}\cos^2\theta - \gamma_{xy}\cos\theta\sin\theta \quad (64)$$

$$\gamma_{12} = 2(-\varepsilon_{xx} + \varepsilon_{yy})\cos\theta\sin\theta + \gamma_{xy}(\cos^2\theta - \sin^2\theta) \quad (65)$$

$$\begin{Bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \frac{1}{2}\gamma_{12} \end{Bmatrix} = \begin{Bmatrix} \cos^2\theta & \sin^2\theta & 2\cos\theta\sin\theta \\ \sin^2\theta & \cos^2\theta & -2\cos\theta\sin\theta \\ -\cos\theta\sin\theta & \cos\theta\sin\theta & \cos^2\theta - \sin^2\theta \end{Bmatrix} \begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \frac{1}{2}\gamma_{xy} \end{Bmatrix} \quad (66)$$

where:

$$\{T\} = \begin{Bmatrix} \cos^2\theta & \sin^2\theta & 2\cos\theta\sin\theta \\ \sin^2\theta & \cos^2\theta & -2\cos\theta\sin\theta \\ -\cos\theta\sin\theta & \cos\theta\sin\theta & \cos^2\theta - \sin^2\theta \end{Bmatrix} \quad (67)$$

is transformation matrix. Rotation of stresses given with Eq. (62) does not depend on material properties. Using Reuter matrix:

$$[R] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \quad (68)$$

it can be written in concise matrix notation:

$$\begin{Bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \gamma_{12} \end{Bmatrix} = [R] \begin{Bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \frac{1}{2}\gamma_{12} \end{Bmatrix} \quad (69)$$

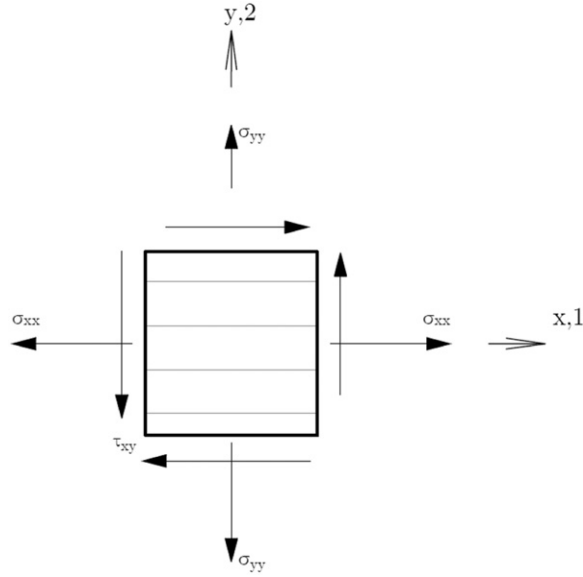


Fig. 23 Special orthotropic lamina.

$$\begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \gamma_{xy} \end{Bmatrix} = [R] \begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \gamma_{xy} \end{Bmatrix} \quad (70)$$

Special Orthotropic Lamina ($\theta = 0^\circ$ or $\theta = 90^\circ$)

Special case where principle material axes coincide with global axes is called specially orthotropic. For this case shown in Fig. 23 stress-strain relations are given as:

$$\begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \gamma_{xy} \end{Bmatrix} = \begin{bmatrix} S_{11} & S_{12} & 0 \\ S_{21} & S_{22} & 0 \\ 0 & 0 & S_{66} \end{bmatrix} \begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{Bmatrix} = [S] \begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{Bmatrix} \quad (71)$$

with:

$$S_{11} = \frac{1}{E_{11}} \quad (72)$$

$$S_{12} = S_{21} = -\frac{\nu_{12}}{E_1} = -\frac{\nu_{21}}{E_{22}} \quad (73)$$

$$S_{22} = \frac{1}{E_{22}} \quad (74)$$

$$S_{66} = \frac{1}{G_{12}} \quad (75)$$

where $[S]$ represents the compliance matrix for specially orthotropic lamina.

Inverting equation stress-strain relations for specially orthotropic lamina:

$$\begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{Bmatrix} = \begin{bmatrix} Q_{11} & Q_{12} & 0 \\ Q_{21} & Q_{22} & 0 \\ 0 & 0 & Q_{66} \end{bmatrix} \begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \gamma_{xy} \end{Bmatrix} = [Q] \begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \gamma_{xy} \end{Bmatrix} \quad (76)$$

where $[Q]$ represents the stiffness matrix for the specially orthotropic lamina, with:

$$Q_{11} = \frac{E_{11}}{1 - \nu_{12}\nu_{21}} \quad (77)$$

$$Q_{22} = \frac{E_{22}}{1 - \nu_{12}\nu_{21}} \quad (78)$$

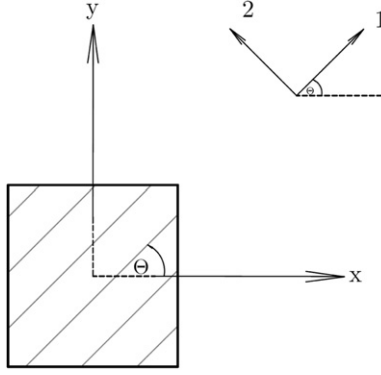


Fig. 24 General orthotropic thin lamina with material and global axes.

$$Q_{12} = Q_{21} = \frac{v_{12}E_{22}}{1 - v_{12}v_{21}} = \frac{v_{21}E_{11}}{1 - v_{12}v_{21}} \quad (79)$$

$$Q_{66} = G_{12} \quad (80)$$

Since Q_{12} and Q_{16} are zero, it may be concluded that when its loading direction coincides with lamina material axes, application of normal stresses produce only normal strains, and application of shear stresses produce pure shear strains.

General Orthotropic Lamina ($\theta \neq 0^\circ$, $\theta \neq 90^\circ$)

The strain-stress relations for a general orthotropic lamina shown in Fig. 24 is given in matrix form:

$$\begin{bmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \gamma_{xy} \end{bmatrix} = \begin{bmatrix} \bar{S}_{11} & \bar{S}_{12} & \bar{S}_{16} \\ \bar{S}_{21} & \bar{S}_{22} & \bar{S}_{26} \\ \bar{S}_{16} & \bar{S}_{26} & \bar{S}_{66} \end{bmatrix} \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{bmatrix} = [\bar{S}] \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{bmatrix} \quad (81)$$

where $[\bar{S}]$ represents the compliance matrix for the lamina.

Elements of the $[\bar{S}]$ matrix may be expressed in terms of the elements of the $[S]$ matrix, for a specially orthotropic lamina, giving engineering constants for an orthotropic lamina loaded in non-principal direction:

$$\bar{S}_{11} = \frac{1}{E_{xx}} = S_{11}\cos^4\theta + (2S_{12} + S_{66})\sin^2\theta\cos^2\theta + S_{22}\sin^4\theta \quad (82)$$

$$\bar{S}_{12} = -\frac{\nu_{xy}}{E_{xx}} = S_{12}(\sin^4\theta + \cos^4\theta) + (S_{11} + S_{22} - S_{66})\sin^2\theta\cos^2\theta \quad (83)$$

$$\bar{S}_{22} = \frac{1}{E_{yy}} = S_{11}\sin^4\theta + (2S_{12} + S_{66})\sin^2\theta\cos^2\theta + S_{22}\cos^4\theta \quad (84)$$

$$\bar{S}_{16} = -m_x = (2S_{11} - 2S_{12} - S_{66})\sin\theta\cos^3\theta - (2S_{22} - 2S_{12} - S_{66})\sin^3\theta\cos\theta \quad (85)$$

$$\bar{S}_{26} = -m_y = (2S_{11} - 2S_{12} - S_{66})\sin^3\theta\cos\theta - (2S_{22} - 2S_{12} - S_{66})\sin\theta\cos^3\theta \quad (86)$$

$$\bar{S}_{66} = \frac{1}{G_{xy}} = 2(2S_{11} + 2S_{22} - 4S_{12} - S_{66})\sin^2\theta\cos^2\theta + S_{66}(\sin^4\theta + \cos^4\theta) \quad (87)$$

where values for S_{11} , S_{12} , S_{22} , S_{66} are defined with Eqs. (72)–(75). Inverting Eq. (81), the stress-strain relations for general orthotropic lamina can be written in form:

$$\begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{bmatrix} = \begin{bmatrix} \bar{Q}_{11} & \bar{Q}_{12} & \bar{Q}_{16} \\ \bar{Q}_{12} & \bar{Q}_{22} & \bar{Q}_{26} \\ \bar{Q}_{16} & \bar{Q}_{26} & \bar{Q}_{66} \end{bmatrix} \begin{bmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \gamma_{xy} \end{bmatrix} = [\bar{Q}] \begin{bmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \gamma_{xy} \end{bmatrix} \quad (88)$$

where $[\bar{Q}]$ represents the transformed stiffness matrix for the lamina. Elements of $[\bar{Q}]$ matrix may be expressed in terms of the elements of the $[Q]$ matrix which allows to compute stresses measured in x-y coordinate system in terms of strains measure in the same system:

$$\bar{Q}_{11} = Q_{11}\cos^4\theta + 2(Q_{12} + 2Q_{66})\sin^2\theta\cos^2\theta + Q_{22}\sin^4\theta \quad (89)$$

$$\bar{Q}_{12} = Q_{12}(\sin^4\theta + \cos^4\theta) + (Q_{11} + Q_{22} - 4Q_{66})\sin^2\theta\cos^2\theta \quad (90)$$

$$\bar{Q}_{22} = Q_{11}\sin^4\theta + 2(Q_{12} + 2Q_{66})\sin^2\theta\cos^2\theta + Q_{22}\cos^4\theta \quad (91)$$

$$\bar{Q}_{16} = (Q_{11} - Q_{12} - 2Q_{66})\sin\theta\cos^3\theta + (Q_{12} - Q_{22} + 2Q_{66})\sin^3\theta\cos\theta \quad (92)$$

$$\bar{Q}_{26} = (Q_{11} - Q_{12} - 2Q_{66})\sin^3\theta\cos\theta + (Q_{12} - Q_{22} + 2Q_{66})\sin\theta\cos^3\theta \quad (93)$$

$$\bar{Q}_{66} = (Q_{11} + Q_{22} - 2Q_{12} - 2Q_{66})\sin^2\theta\cos^2\theta + Q_{66}(\sin^4\theta + \cos^4\theta) \quad (94)$$

It should be noted that elements $\bar{S}_{16}$ and $\bar{S}_{26}$ or $\bar{Q}_{16}$ and $\bar{Q}_{26}$ are not zero in contrast to special lamina case and represent extension-shear coupling, because of what for a general orthotropic lamina, i.e., application of normal stresses produce normal as well as shear strains. Also $\bar{S}_{16}$, $\bar{S}_{26}$, $\bar{Q}_{16}$ and $\bar{Q}_{26}$ definition involves linear combinations of four elements $\bar{S}_{11}$, $\bar{S}_{22}$, $\bar{S}_{12}$ and $\bar{S}_{66}$, which reduces number of independent values. Elements of $[\bar{S}]$ and $[\bar{Q}]$ are expressed in terms of the properties in the principal material directions, E_{11} , E_{22} , G_{12} and ν_{12} .

Fig. 25 shows examples of the dependence of the elastic constants E and G on the angle of orientation of the fibers θ given with Eqs. (82) and (87). When changing between the load angle and the fiber, the stiffness of the composite decreases sharply with the change in the angle of θ , while the shear stiffness has a maximum in a direction of 45° relative to the fiber axis Table 5.

Detailed derivations of presented equations may be found in various books, (Agarwal *et al.*, 2017; Mallick, 1988; Barbero, 2017; Kojic *et al.*, 1998).

Example

Calculate stiffness in 1-direction for a ply carbon-epoxy composite. Given characteristics $E_1 = 175$ MPa, $E_2 = 8$ MPa, $G_{12} = 5$ MPa, $\nu_{12} = 0.3$, $\theta = 24^\circ$ in 1-direction. Calculate stiffness in 1-direction.

Strain induced in 1-direction by strain in 2-direction:

$$\nu_{21} = \nu_{12} \frac{E_2}{E_1} \quad (95)$$

Compliance matrix:

$$\mathbf{S} = \begin{bmatrix} \frac{1}{E_1} & -\frac{\nu_{21}}{E_2} & 0 \\ -\frac{\nu_{21}}{E_1} & E_2 & 0 \\ 0 & 0 & \frac{1}{G_{12}} \end{bmatrix} \quad (96)$$

With $m = \cos\theta$ and $n = \sin\theta$:

$$\mathbf{T} = \begin{bmatrix} m^2 & n^2 & 2mn \\ n^2 & m^2 & -2mn \\ -mn & mn & m^2 - n^2 \end{bmatrix} \quad (97)$$

Reutens matrix:

$$\mathbf{R} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \Rightarrow \mathbf{R}^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{1}{2} \end{bmatrix} \quad (98)$$

Further:

$$\mathbf{t} = \mathbf{R}^{-1}\mathbf{T}\mathbf{R} = \begin{bmatrix} m^2 & n^2 & mn \\ n^2 & m^2 & -mn \\ -2mn & 2mn & m^2 - n^2 \end{bmatrix} \Rightarrow \mathbf{t}^{-1} = \mathbf{R}\mathbf{T}^{-1}\mathbf{R}^{-1} \quad (99)$$

Compliance matrix of θ degree:

$$\bar{\mathbf{S}} = \mathbf{R}\mathbf{T}^{-1}\mathbf{R}^{-1}\mathbf{S}\mathbf{T} = \mathbf{t}^{-1}\mathbf{S}\mathbf{T} = 10^{-6} \begin{bmatrix} 0.0345 & -0.0108 & -0.0601 \\ -0.0108 & 0.1144 & -0.0279 \\ -0.0601 & -0.0279 & 0.1636 \end{bmatrix} \quad (100)$$

Stiffness matrix:

$$\bar{\mathbf{D}} = \bar{\mathbf{S}}^{-1} = \begin{bmatrix} 1.26 & 0.244 & 0.509 \\ 0.244 & 0.138 & 0.114 \\ 0.509 & 0.114 & 0.269 \end{bmatrix} 10^8 \quad (101)$$

Using Eq. (100) stiffness in 1-direction can be calculated using:

$$E_1 = \frac{1}{0.0345 \cdot 10^{-6}} = 2.89 \cdot 10^9 \text{ MPa} \quad (102)$$

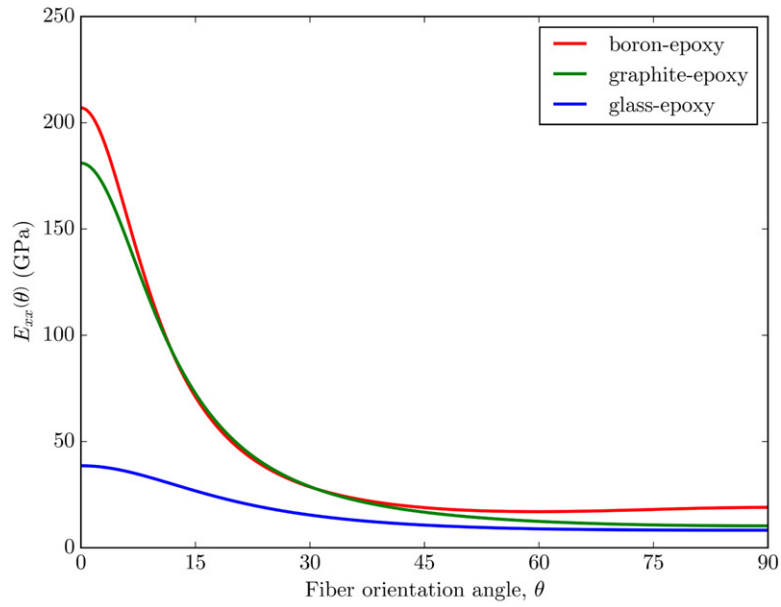
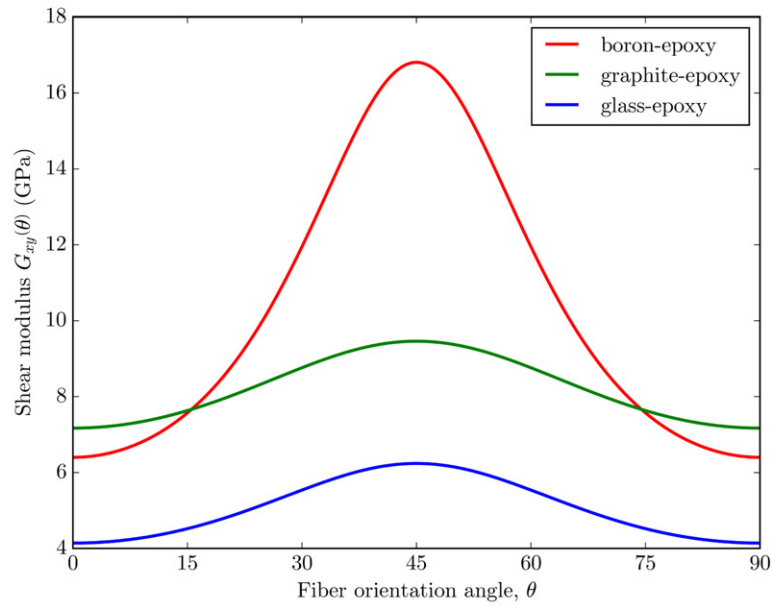

 (a) $E_{xx}(\theta)$

 (b) $G_{xy}(\theta)$
Fig. 25 Dependence of elastic and shear moduli on the angle. (a) $E_{xx}(\theta)$. (b) $G_{xy}(\theta)$.

Table 5 Material properties of various composites used in 25

Composite	E_1	E_2	G_{12}	ν_{12}
Boron-epoxy	207	19	6.4	0.21
Graphite-epoxy	181	10.3	7.17	0.28
Glass-epoxy	38.6	8.27	4.14	0.26

FEM Modeling of FRC

Due to the heterogeneous structure and application of composite materials, the use of knowledge from several fields is imposed: elasticity, finite element method, strength of materials, anisotropy, micro-mechanics (Jones, 1999).

Hardware development in the last few decades has significantly accelerated and shortened the time required for modelling and analysis of structures. For the previously presented equations, the script programs MATLAB (MATLAB, 2010) and Python (Van et al., 2009) are especially suitable, enabling simple analysis of the equations of micro-mechanics of constituents and laminae. Also, advanced commercial software packages contain and develop special modules and plug-ins for structural analysis of composites (ABAQUS, 2009; COMSOL Multiphysics, 1998). Due to the development and industrial application of composites, their analysis is attracting increasing attention of the academic community, and thus university software such as CADEC and PAK (Kojic et al., 1995) is emerging.

The development of calculation methods, and in particular FEA, enables successful application in linear and non-linear structural analysis. Non-linear analysis includes geometric and material non-linearity, stability analysis and post critical behaviour of structures. In addition, FRCs can exhibit anisotropic, (Car et al., 2000) orthotropic, (Kojic et al., 1996) or even behaviors such as porous structures (Sharma et al., 2019). The advantage of using FEM in the calculation of composite structures is that each finite element may have different material characteristics, and within the element can be taken into account the characteristics of individual layers. More recently, a number of software packages have been developed that have been successfully implemented in solving the above problems of composite structures.

This section provides a brief overview of FEM theory using software package PAK Multiphysics (PAK-S and PAK-T) (Kojic et al., 1995; Dunić et al., 2016) for Finite Element Analysis (FEA).

Basic Stress-Strain Relations in FEM for Composite Structures

Modelling finite element structures involves splitting the structure into finite elements and using interpolation to displacements and other values within the element and relate them to the nodal values. Based on the adopted interpolation using the principle of virtual displacements, we arrive at the equilibrium equation of the element or structure, which for non-linear analysis has the following form:

$$\mathbf{F} = \mathbf{K}\mathbf{u} \quad (103)$$

Where $\mathbf{K}$, $\mathbf{u}$ and $\mathbf{F}$ represent stiffness matrix, vector of unknown nodal forces and vector of external known nodal forces, respectively. Solving the system of equations results in nodal displacements followed by deformations and stresses. In non-linear analysis, an incremental analysis procedure is used using equilibrium iterations according to the following equation.

$$\left({}^{t+\Delta t}\mathbf{K}_L^{(i-1)} + {}^{t+\Delta t}\mathbf{K}_{NL}^{(i-1)} \right) \Delta \mathbf{U}^{(i)} = {}^{t+\Delta t}\mathbf{R}^{(i-1)} + {}^{t+\Delta t}\mathbf{F}^{(i-1)} \quad (104)$$

Where ${}^{t+\Delta t}\mathbf{K}_L^{(i-1)}$, ${}^{t+\Delta t}\mathbf{K}_{NL}^{(i-1)}$, ${}^{t+\Delta t}\mathbf{R}^{(i-1)}$, ${}^{t+\Delta t}\mathbf{F}^{(i-1)}$, $\Delta \mathbf{U}^{(i)}$, are linear part of stiffness matrix of system, non-linear part of stiffness matrix of system, external forces vector at $t + \Delta t$, internal forces vector and displacement increment vector, respectively. In Eq. (104) $t + \Delta t$ and (i) k.

Stiffness matrix $\mathbf{K}$ in Eq. (103) and matrix $\mathbf{K}_L$ in Eq. (104) are given with:

$$\mathbf{K} = \int_V \mathbf{B}^T \mathbf{C} \mathbf{B} dV \quad (105)$$

Matrix $\mathbf{B}$ in equation represents relation between displacement increment in non-linear analysis and deformation in arbitrary point of finite element.

Matrix $\mathbf{C}$ represents constitutive matrix, relation between stress and deformation. In case of composite materials matrix $\mathbf{C}$ includes anisotropic characteristics of material by defining relation for main material orientations for given layer, and is later transformed to global coordinate system.

In the case of material non-linear analysis, the stresses at the integration point are calculated by the integration of constitutive relations defining the elasto-plastic behaviour of the material using the yield condition and the proper hardening law.

Vector of internal forces in Eq. (104) is given with relation:

$$\mathbf{K} = \int_V \mathbf{B}^T \mathbf{C} \mathbf{B} dV \quad (106)$$

For elasto-plastic analysis stress vector $\boldsymbol{\sigma}$ is given with:

$$\boldsymbol{\sigma} = \mathbf{C} \left({}^{t+\Delta t}\mathbf{e}^e - {}^{t+\Delta t}\mathbf{e}^p \right) \quad (107)$$

For the case of thermoplasticity relation is given in form:

$$\boldsymbol{\sigma} = \mathbf{C} \left({}^{t+\Delta t}\mathbf{e}^e - {}^{t+\Delta t}\mathbf{e}^p - {}^{t+\Delta t}\mathbf{e}^{th} \right) \quad (108)$$

Where ${}^{t+\Delta t}\mathbf{e}^{th}$ represent thermal strains for corresponding temperature field for given time increment $t + \Delta t$. Temperature field is calculated by solving heat conduction problem or is determined by experiment.

In elasto-plastic analysis for orthotropic materials generalized Hill's yield condition with material hardening is given in Kojic *et al.* (1996) and Kojic (1996). Here basic relations of material model and stress integration are presented.

The flow condition, which takes into account the translation of the flow surface in the stress space and the change in the shape of the surface, can be written in the following form:

$$f_y = \frac{1}{2} \hat{\mathbf{S}}^T \mathbf{N} \hat{\mathbf{S}}' - \frac{1}{3} \hat{\sigma}_y^2 = 0 \quad (109)$$

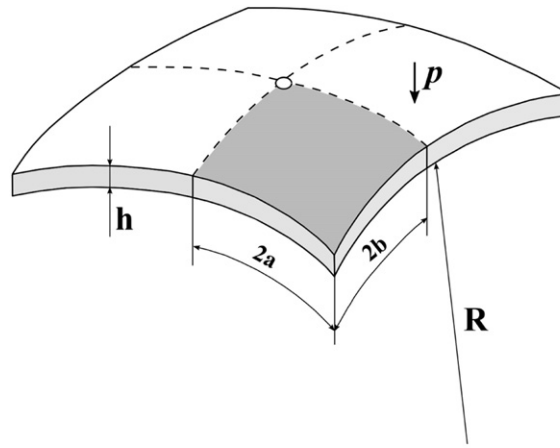
where $\hat{\mathbf{S}}$ represents yield surface radius while $\hat{\mathbf{S}}'$ takes into account double shear stress values. $\mathbf{N}$ is shape coefficient matrix, and $\hat{\sigma}_y^2$ is yield stress. Yield stress and shape coefficients are given in terms of equivalent plastic strain $\bar{\epsilon}_a^p$. Yield stress is usually given in form (Kojic *et al.*, 1996):

$$\hat{\sigma}_y = \sqrt{\left\{ \frac{1}{2} \left[\frac{1}{3} (X^2 + Y^2 + Z^2) + Y_{xy}^2 + Y_{yz}^2 + Y_{xz}^2 \right] \right\}} \quad (110)$$

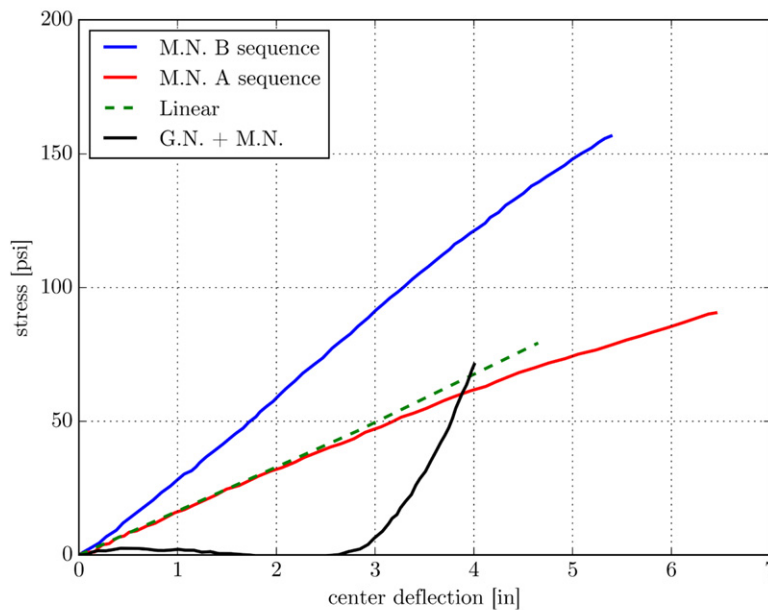
where $X, Y, \dots, Y_{xz}$ are yield stresses corresponding to uniaxial stress states for material directions in lamina. It is possible to use analytical form of yield stress. Ramberg-Osgood form is given with:

$$X = X_0 + C_x (M \bar{\epsilon}_a^p)^{n_x} \quad (111)$$

where X_0 is initial yield stress for first material direction, C_x, n_x are material constants and $0 \leq M \leq 1$ is mixed hardening parameter.



(a) schematic representation of problem



(b) force-displacement curve

Fig. 26 Two-layered pipe with orthotropic material ($\pm 45^\circ$) subjected to two forces. (a) schematic representation of problem. (b) force-displacement curve.

Yield surface position, because of the kinematic hardening is given with:

$$dz = (1 - M)C^P de^P \quad (112)$$

Matrix C^P takes into account plastic moduli of E^P for corresponding yield curve, and de^P is plastic strain increment.

With given yield condition and previous equations radius of yield surface at the end of the time step Δt is given with:

$$\hat{S} = \left\{ \Delta \lambda \left[C'^E + (1 - M) \bar{C}^P \right]^{t+\Delta t} N + I \right\}^{t+\Delta t} \hat{S}^E \quad (113)$$

where $\hat{S}^{t+\Delta t}$ is radius of yield surface for elastic solution, C'^E matrix which gives relation between elastic deviatoric stress and strain, $\bar{C}^P$ is weight function C^P for time step, $\Delta \lambda$ scalar parameter to be determined.

Tangent stiffness matrix, to provide quadratic convergence, is given in form:

$${}^{t+\Delta t}C_{EP} = \frac{\partial^{t+\Delta t}\sigma}{\partial^{t+\Delta t}e} \quad (114)$$

The Eqs. (113)–(114) are solved using GPM given in Kojic *et al.* (1996) and Kojic (1996).

Calculation of Temperature Field in Composite Structures

The conduction of heat through solids is described by Fourier's law, which in the case of an anisotropic body is given with:

$$\frac{\partial}{\partial x} \left(K_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial T}{\partial z} \right) + q = \rho c \frac{dT}{dt} \quad (115)$$

where K_x , K_y and K_z are heat conduction coefficients for three orthogonal directions, non equal for anisotropic material in general case, q is source volume per unit volume, ρ is density, c is specific heat for material, t is time, $T = T(x, y, z, t)$ is temperature for arbitrary body point.

In the case of nonlinear material behavior, material characteristics can be given as functions of temperature. Eq. (108) can be solved by applying (FEM) for arbitrary boundary conditions which include:

- known temperatures on the body contour part
- the heat transfer described by the equation $q_h = h(T - T_s)$
- radiation on the part of the contour described by the relation $q_r = h_r(T_r - T_s)$

where h is coefficient of heat transfer, T is temperature, T_s temperature of the body surface, T_r is temperature of radiation source, with radiation coefficient as nonlinear function of wall temperature $h_r = \varepsilon(T_r^2 + T_s^2)(T_r + T_s)$.

In-house developed software for coupled thermo-mechanical problems, PAK(PAK-T), (Kojic *et al.*, 1995) is based on finite element method, allows solving nonlinear coupled problems using an incremental procedure and equilibrium iterations.

Examples

Freely supported spherical shell loaded with surface pressure

The double-curved shell with the geometric characteristics shown in the figure was analyzed for two sequences of material layers $A(0/90^\circ)$ and $B(\pm 45^\circ)$. Material parameters used in example:

$E_{11} = 3.0 \times 10^7$	$E_{22} = 2.7 \times 10^6$	$E_{33} = 2.7 \times 10^6$
$G_{12} = 0.7 \times 10^6$	$G_{23} = 0.28 \times 10^6$	$G_{31} = 0.7 \times 10^6$
$\nu_{12} = 0.21$	$\nu_{23} = 0.21$	$\nu_{31} = 0.21$
$X^0 = 1.2 \times 10^5$	$Y^0 = 8.0 \times 10^3$	$Z^0 = 8.0 \times 10^3$
$Y_{xy}^0 = 1.05 \times 10^4$	$Y_{yz}^0 = 1.05 \times 10^4$	$Y_{zx}^0 = 1.05 \times 10^4$
$C_x = 2.63 \times 10^7$	$C_y = 2.3 \times 10^6$	$C_z = 2.3 \times 10^6$
$C_{xy} = 3.4 \times 10^5$	$C_{yz} = 3.4 \times 10^5$	$C_{zx} = 3.4 \times 10^5$

The results shown in the figure show the dependence of the displacement forces for linear (L), material nonlinear (MNO) and elasto-plastic geometric nonlinear analysis (MN + GL). Fig. 26 shows that the deflections for (MN + GL) are higher than for the linear case (L) and the material nonlinear case due to the snap-through effect.

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Material Modeling of Concrete

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Introduction

The modern history of concrete production is approximately 150 years old. Although cement production is linked to the high emission of CO_2 , the forecast is that concrete will remain the most extensively consumed engineering material for the civil engineering structures in the world (Schneider, 2019; Gagg, 2014). The main topic of the International Federation for Structural Concrete (fib) Symposium in 2020 was planned to be “Concrete Structures for Resilient Society” which includes Analysis and Design topics.

Today, the concrete structures are designated by standards such as Eurocodes or ModelCode 2010 (Marinkovic and Pecic, 2018). Buildings, infrastructure, and transport systems are structures of great importance that need to satisfy a proper safety level. The accurate and efficient simulation is essential for the safety of concrete structures such as dams, roads, bridges, water tanks, towers, etc. The safety analysis considers the prediction of remaining service life and the requirement for reconstruction or maintenance of concrete structures. One possibility is developing an appropriate mathematical model based on the research of concrete structure behavior capable of simulating the response under specific loading and boundary conditions. The engineers and researchers developed various constitutive relations and approaches to model and predict the behavior of the concrete structures. Many solutions are already implemented into Finite Element Method (FEM) software that has been used for years as an engineering tool for efficient and accurate structural analysis. This is important because of the production of concrete structures increases and the requirements for concrete structures such as reliability, safety, functionality, and durability, but also robust design and sustainability, are very high (Marinkovic and Pecic, 2018).

State of the Art in Material Modeling of Concrete

Concrete is cohesive-frictional material. The concrete behavior is linear for small strain at a macro level. Based on experimental observations, the stress-strain relation has a non-linear character in tension and compression above the critical strength value. In this stage, inelastic strains and concrete deterioration are visible. The failure of a concrete structure is associated with the microcracking processes such as loss of cohesion at the mortar–aggregate interface, slip along the cracking surfaces and crushing (Lowes, 1999).

There are a variety of concrete constitutive models proposed to simulate behavior for a specific loading and boundary conditions (Babu *et al.*, 2005): empirical models, linear and nonlinear elastic, plasticity models, endochronic models, fracturing models, continuum damage mechanics (CDM) models, and micromechanical models. The three approaches are the most attractive (Lee, 1996): discrete crack model, smeared crack model, and plasticity-based crack model. Constitutive models should be developed and implemented to simulate macroscopic behavior. Similar to other types of material, the concrete constitutive relations have to be based on continuum mechanics and thermodynamics. The modeling approaches can be classified as micromechanical, phenomenological or micro-macro models. The micromechanical strategy allows a better perception of the material behavior, but the large-scale application is more complex (ADINA, 2012). Phenomenological models are more convenient for engineering application, but also, development and implementation of the model is simple.

The discrete crack models recognize the crack as geometrical discontinuity. The initiation of cracking process and crack propagation are interesting phenomena for simulation (Lee, 1996), but also post-ultimate behavior and cyclic loading response (Kotsovos and Pavlović, 1995). The crack initiation is forming of microcracks, while the crack propagation represents their interconnection (Lee, 1996). Crack initiation is managed by force at the crack tip. If the force exceeds the tensile strength, the material is separated and this process continues (Borst *et al.*, 2004). Such models are inefficient and have low accuracy in the case of many cracks in the material (Lee, 1996).

The smeared crack strategy recognizes the crack initiation and development as a continuum process. Many small cracks form one dominant crack inducing degradation of material's stiffness and strength. The stress state is employed to determine the criterion of crack initiation. For example, major principle stress can be compared to tensile strength (Borst *et al.*, 2004). The very important advantage of this approach is a simple numerical implementation.

The plasticity-based crack model is controlled by a plastic yielding function which determines the crack propagation. The cornerstones of plasticity models are (Kojic and Bathe, 2005): yield criteria, flow rule, and hardening-softening rule. One of the disadvantages is a difficult calibration of material parameters. Lubliner *et al.* (1989) noticed that the model is complicated and possibly unstable. The most popular and the most interesting models are plasticity-based models coupled with CDM. Damage mechanisms that enhance the plasticity models are strain softening and stiffness degradation (Nguyen, 2005). The solution is offered by the relationship between irrecoverable strains and damage parameters. Localization of deformation can be solved by regularization techniques (Nguyen, 2005).

Plasticity Based Models

The concrete is viscous-elastic-plastic composite material (Nguyen, 2005). Plasticity models are very popular for metals, and the advantages can be used for concrete modeling. Above a maximum strength value of the concrete, cracking or crushing occurs in a

nonlinear manner resulting in inelastic strains. This should be considered under specific loading conditions such as dynamic, impact or cyclic loading.

Total strain decomposition is applied to specify the value of inelastic strain (Nguyen, 2005). Decomposition of total strain tensor $\boldsymbol{\varepsilon}$ on elastic $\boldsymbol{\varepsilon}_e$ and plastic part $\boldsymbol{\varepsilon}_p$ is (Kojic and Bathe, 2005; Willam, 2003):

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_p. \quad (1)$$

Stress tensor $\boldsymbol{\sigma}$ is related to the elastic strain as (Kojic and Bathe, 2005):

$$\boldsymbol{\sigma} = \mathbf{C} : \boldsymbol{\varepsilon}_e, \quad (2)$$

$$\boldsymbol{\sigma} = \mathbf{C} : (\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_p), \quad (3)$$

where $\mathbf{C}$ is an elastic matrix. All plasticity-based models consist of the following relations:

- (1) Yield criteria define the stress state of the material when the plastic strain occurs. In general, the yield function is defined as:

$$F(\boldsymbol{\sigma}) = 0. \quad (4)$$

In relation to stress invariant, the yield function can be written as:

$$F(I_1, J_2, J_3) = 0, \quad (5)$$

where I_1 is the first invariant of the stress tensor, and J_2 , and J_3 are the second and the third invariant of the deviatoric stress tensor. Yield surface can be related to hydrostatic pressure (i.e., Mohr-Coulomb, Drucker-Prager) or it can be independent of hydrostatic pressure (i.e., Tresca, Von-Mises) (Nguyen, 2005). If the concrete is considered as isotropic material, the yield hardening function is not dependent on the stress direction. The important characteristic of yield function is the number of parameters.

- (2) Yield hardening rule defines the plastic flow direction. The plastic strain increment vector $\mathbf{s}$ is described as partial derivative of the plastic potential function Q over the stress tensor (Willam, 2003):

$$\mathbf{s} = \frac{\partial Q}{\partial \boldsymbol{\sigma}}. \quad (6)$$

When the plastic potential function Q is the same as the yield function F , we have an associated flow rule which is unsuitable for concrete models, because the concrete displays volume change (Babu *et al.*, 2005).

- (3) Hardening or Softening rule is the law which defines the change of yield surface when plastic strain occurs. It is also recognized as the evolution of yield surface. It can be isotropic, kinematic and mixed hardening (Babu *et al.*, 2005; Willam, 2003).

Damage and Degradation

Material damage and stiffness degradation are introduced by the concept of “effective stress” (Lemaitre and Desmorat, 2005). The effective stress $\bar{\boldsymbol{\sigma}}$ is defined as (Lemaitre, 1992):

$$\bar{\boldsymbol{\sigma}} = \frac{\boldsymbol{\sigma}}{1 - d}, \quad (7)$$

where d is a degradation variable that describes material deterioration (Borst *et al.*, 2004). The strain equivalence principle (Lemaitre, 1992; Simo and Ju, 1987a,b) defined that effective stress should be used in the constitutive relations for damaged material strain instead of usual stress for virgin material strain:

$$\bar{\boldsymbol{\varepsilon}} = (1 - d)\boldsymbol{\varepsilon}. \quad (8)$$

This explained the concept of effective stress. Coupling between the degradation and elasticity is considered on uniaxial loading case:

$$\sigma = (1 - d)E\varepsilon_e, \quad (9)$$

where E is the Young modulus, and ε_e is the elastic strain.

The damage variable κ can be represented as scalar, vector, or tensor (Babu *et al.*, 2005; Lee, 1996). The scalar damage variable is preferred due to a simple formulation, an easy numerical implementation, and a possibility of parameter identification. The value of damage and degradation are between zero (undamaged) and unity (totally damaged). The evolution law of damage can be separated into three categories (Nguyen, 2005): Imposed damage evolution laws, Damage evolution laws obtained from a dissipation potential, Implicitly defined damage evolution laws.

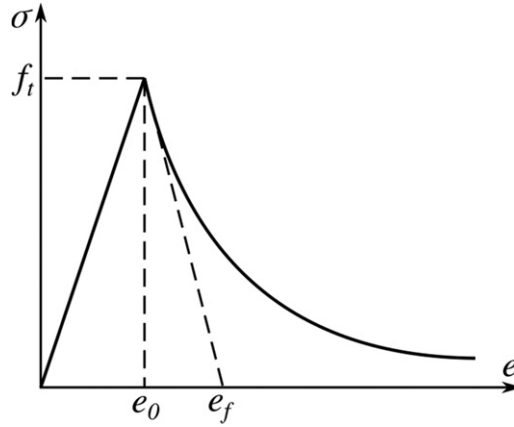


Fig. 1 Softening law.

The example of the first group is a curve based on experimental uniaxial behavior (Grassl and Jirásek, 2006):

$$d = g(\kappa) = \begin{cases} 0 & \kappa < \kappa_0 \\ 1 - \frac{e_0}{\kappa} \exp\left(\frac{\kappa - e_0}{e_f - e_0}\right) & \kappa \geq \kappa_0 \end{cases}, \quad (10)$$

where e_0 is the strain at maximum stress and e_f is a material constant that defines a slope of softening (Fig. 1). Based on experimental results, the damage is responsible for softening the material and the degradation of elastic characteristics. There are two types of coupling between damage and plasticity, as shown in Fig. 2 (Nguyen, 2005):

- (1) Implicit coupling – Function of material strength with respect to damage variable is implemented into the yield or damage criteria.
- (2) Indirect coupling – Damage or yield functions are used to control the dissipation process.

Plasticity-Damage Models

Plasticity-damage models simulate decreasing of stiffness and strength of the material in relation to damage parameter. To define such a model, it is necessary to provide: damage surface, damage loading function, and consistency condition (Nguyen, 2005). The different concrete behavior in tension and compression can be considered by two separate damage variables. It is also possible to separate stress and strain in positive and negative parts and to define two loading surfaces. Some of the best-known models will be presented below.

Lubliner *et al.*

Lubliner *et al.* (1989) used plasticity formulation with an internal variable. They presented a new yield function. The concrete behavior was considered as nonlinear because of stiffness degradation or plastic strains occurrence. The yield function is based on Mohr-Coulomb or Drucker-Prager criteria (Lubliner *et al.*, 1989):

$$F(\sigma) = c, \quad (11)$$

where F is the yield function which depends on stress components, and c is the cohesion. The evolution laws of cohesion and hardening variable are related to the damage variable κ . Total damage corresponds to the cohesion, which has the initial value of compression yield strength f_{c0} . The flow rule is (Lubliner *et al.*, 1989):

$$\dot{\epsilon}_p = \dot{\lambda} \mathbf{g}, \quad (12)$$

where $\dot{\lambda}$ is the plastic loading factor and $\mathbf{g}$ is the normal vector to the plastic potential G . The damage κ is correlated with the plastic strain as follows (Lubliner *et al.*, 1989):

$$\dot{\kappa} = \mathbf{h} \dot{\epsilon}_p \quad (13)$$

The damage variable κ_{Ξ} is defined as (Lubliner *et al.*, 1989):

$$\kappa_{\Xi} = \frac{1}{g_{\Xi}} \int_0^{\epsilon^p} \sigma d\epsilon_p \quad (14)$$

for $\Xi = c, t$, where c and t denote compression and tension, respectively. Relation $\sigma_{\Xi} = f_{\Xi}(\kappa_{\Xi})$ is defined for both tension and compression. Also, the details about the significance of g_{Ξ} are explained in Lubliner *et al.* (1989). In Fig. 3, the area below the curve

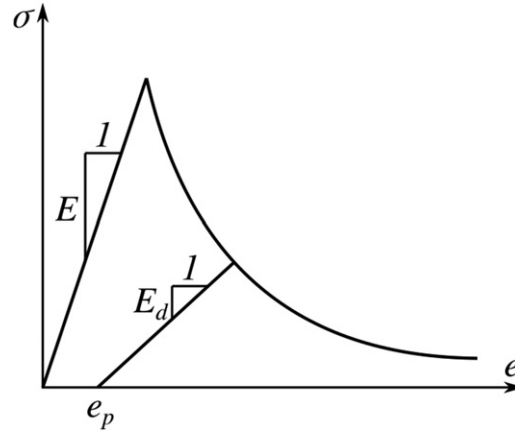


Fig. 2 Coupling between damage and plasticity.

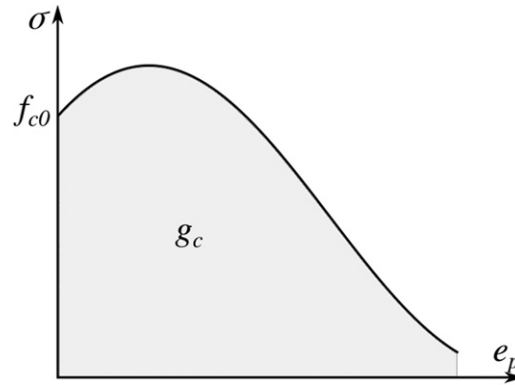


Fig. 3 Uniaxial stress-plastic strain relationship in compression.

represents the specific fracture energy g_c . The multiaxial stress state is taken into account by weight factor $r(\sigma)$ (Lubliner *et al.*, 1989):

$$\dot{\kappa} = \frac{r(\sigma)}{g_t} f_t(\kappa) \dot{e}_{p1} + \frac{1-r(\sigma)}{g_c} f_c(\kappa) \dot{e}_{p3} \quad (15)$$

The yield surface is adopted as follows (Lubliner *et al.*, 1989):

$$F(\sigma) = \frac{1}{1-\alpha} [\sqrt{3}I_2 + \alpha I_1 + \beta \langle \sigma_{\max} \rangle - \gamma \langle \sigma_{\max} \rangle] \quad (16)$$

where α, β, γ are constants. The Mohr-Coulomb yield function is employed as plastic potential function G (Lubliner *et al.*, 1989) as follows:

$$G(\sigma, \psi) = \frac{I_1}{3} \sin \psi + \sqrt{I_2} \left(\cos \theta - \frac{\sin \theta \sin \psi}{\sqrt{3}} \right), \quad (17)$$

where ψ is the angle of dilatancy.

Lee and Fenves

Lee and Fenves (1998) model is formulated for the earthquake simulation of dams. Damage variables are separated into tension and compression loading cases. They provided the possibility to simulate large crack opening displacement. The combined yield-failure surface is defined related to damage variables:

$$f_d(\sigma, \kappa) = 0 \quad (18)$$

where $\kappa = \{\kappa_t, \kappa_c\}^T$ is damage variables vector. Opening and closing of cracks follow the rule (Lee and Fenves, 1998):

$$d = 1 - (1 - d_c(\kappa_c))(1 - s d_t(\kappa_t)) \quad (19)$$

where $s = s(\sigma)$ is the stiffness recovery. Flow rule is defined as (Lee and Fenves, 1998):

$$\varphi = \sqrt{2J_2} + \alpha_p I_1, \quad (20)$$

where α_p controls the dilatancy. More details can also be found in [Rakić et al. \(2019\)](#).

Faria et al.

The model introduced by [Faria et al. \(1998\)](#) is a plasticity-based model with two scalar damage variables. The stress is decomposed into the tension $\bar{\sigma}^+$ and compression part $\bar{\sigma}^-$. Helmholtz free energy potential divided into the tensile and compressive part is used to establish a constitutive law ([Faria et al., 1998](#)):

$$\psi = (1 - d_t)\psi_0^+ + (1 - d_c)\psi_0^- \quad (21)$$

Damage criteria are defined independently for tension and compression via equivalent stresses τ^+ and τ^- defined in ([Faria et al., 1998](#)):

$$g^+ = \tau^+ - r^+ = 0 \quad (22)$$

$$g^- = \tau^- - r^- = 0 \quad (23)$$

where r^+ and r^- are thresholds related to the dimension of the damage surface. Constitutive law is proposed in the following form ([Faria et al., 1998](#)):

$$\sigma = (1 - d_t)\sigma^+ + (1 - d_c)\sigma^- \quad (24)$$

where d^+ and d^- are tensile and compressive damage variables, respectively. The model was proposed for the massive concrete structures. It was possible to capture the stiffness degradation and recovering. They also included rate sensitivity into the model.

Concrete Models in FEM Software

The various FEM software (Abaqus, Adina, Ansys, LS-Dyna) have implemented the constitutive models as the solution for the efficient simulation of concrete structures behavior. Taking into account specific application and needs, like analysis of concrete dams, the following models are presented:

ABAQUS

[ABAQUS \(2013\)](#) has three models available for simulation:

- (1) Concrete smeared cracking in Abaqus/Standard is designed for monotonic loading conditions. Cracking occurs in tension while crushing in compression. For this model, it is possible to use beams, trusses, shells, and solids, but also to include the reinforcement. Cracking is related to stress which approaches the "crack detection surface". It is considered as the smeared crack model because it doesn't track individual cracks. The post-failure behavior is modeled with the tension stiffening by stress-strain relation or by fracture energy cracking criterion.
- (2) Cracking model for concrete in Abaqus/Explicit considers brittle behavior of the structure. In this model, compressive loading is linearly elastic and the tensile cracking is dominant. This model is also good for modeling ceramics or brittle rocks.
- (3) Concrete damage plasticity in both Abaqus/Standard and Abaqus/Explicit assumes scalar damage variable and arbitrary loading conditions. It is possible to simulate cyclic loading behavior. The degradation of the stiffness is included in tension and compression. This model is based on [Lee and Fenves, 1998](#).

ADINA

Data fitted (DF) concrete model ([ADINA, 2012](#)) is implemented into the ADINA software. Based on the experimental test results, the model is simple, effective, and applicable to static and dynamic conditions (earthquakes) ([Kotsovos and Pavlović, 1995](#); [Kotsovos and Spiliopoulos, 1998](#)). This model is used in many cases ([Bathe et al., 1989](#)), but one of the well-known applications in literature is a gravity concrete dam analyzed by [Carpinteri et al. \(1992\)](#), where the obtained results are compared with the experiment.

The model is based on an experimental stress-strain curve for both tension and compression. An experimentally determined three-dimensional failure surface is applied to describe failure (cracking or crushing). The smeared crack approach is used as a post-failure type of response, which gives the possibility to close and to open cracks. The material parameters can be expressed concerning the strength in compression.

ANSYS

ANSYS ([Kohnke, 1999](#)) uses Willam-Warnke failure criterion ([Willam and Warnke, 1974](#)) for analysis of multi-axial stress states. This criterion depends on five material parameters. The material model can simulate cracking in tension and crushing in

compression defined by a failure surface. For a concrete model definition, tension strength of concrete and shear transfer coefficients need to be defined. The concrete model can also simulate plastic behavior using the Drucker-Prager failure surface.

LS-DYNA

LS-DYNA has several models for the simulation of the concrete structure, but the three most used are Mat Winfrith Concrete (MAT084), Mat CSCM Concrete (MAT159), and MAT CDPM (MAT273).

Mat Winfrith Concrete (MAT084) (Hallquist, 2006), or so-called the Winfrith concrete model, is intended for simulation of impact loading of Reinforced Concrete (RC) structures. It is based on the four-parameter Ottosen model (Ottosen, 1977; Zhang *et al.*, 2020) yield function:

$$Y(I_1, J_2, J_3) = \frac{\alpha J_2}{f_c} + \frac{\lambda \sqrt{J_2}}{f_c} + \frac{b I_1}{f_c} - 1 \quad (25)$$

where $\lambda = \lambda(\cos 3\theta, k_1, k_2)$ and α, b, k_1, k_2 are constants.

Mat CSCM Concrete (MAT159) (Hallquist, 2006; Murray, 2007) is so-called Continuous Surface Cap Model for concrete intended for use in the roadside safety simulations. The three-dimensional yield surface is defined as (Hallquist, 2006):

$$Y(I_1, J_2, J_3) = J_2 - R^2(J_3)F_f^2(I_1)F_c(I_1, \kappa) \quad (26)$$

where $F_f(I_1)$ is the shear failure surface, $F_c(I_1, \kappa)$ is the hardening cap with κ as the hardening parameter, and $R(J_3)$ is the invariant reduction factor.

The concrete damage plasticity constitutive model MAT CDPM (MAT273) is based on published papers: Grassl and Jirásek (2006) and Grassl *et al.* (2013). A one-scalar damage variable is combined with an effective stress plasticity model. After the peak stress value, perfect plasticity was applied while softening was taken into account by the damage part. This model is extended by Grassl *et al.* (2013) by three main changes:

- (1) The contribution of plasticity and damage is controlled by hardening in the plasticity part after the peak stress,
- (2) Two separate damage parameters are proposed for tension and compression,
- (3) Damage evolution is related to a strain rate.

The yield function is defined as in Grassl *et al.* (2013):

$$f_p(\bar{\sigma}_v, \bar{\rho}, \bar{\theta}, \kappa_p) = \left\{ [1 - q_{h1}(\kappa_p)] \left(\frac{\bar{\rho}}{\sqrt{6}f_c} + \frac{\bar{\sigma}_v}{f_c} \right)^2 + \sqrt{\frac{3}{2}} \frac{\bar{\rho}}{f_c} \right\}^2 + m_0 q_{h1}^2(\kappa_p) q_{h2}(\kappa_p) \left[\frac{\bar{\rho}}{\sqrt{6}f_c} r \cos \bar{\theta} + \frac{\bar{\sigma}_v}{f_c} \right] - q_{h1}^2(\kappa_p) q_{h2}^2(\kappa_p) \quad (27)$$

where σ_v is the volumetric effective stress, ρ is the norm of the deviatoric effective stress, θ is the Lode angle, κ_p is the hardening variable, f_c is the uniaxial compression strength, and m_0 is the friction coefficient.

Conclusions

Considering the presented overview, it is obvious that the material modeling of concrete is a really extensive scientific field with many open questions, but also many proposed answers. The scientific community offered the solutions at the theory level, but also successfully implemented some of them into the FEM software (in-house or a commercial one). From the engineering point of view, the selection of an appropriate solution depends on the many aspects: the scale of the problem, availability of material parameters, type of loading and boundary conditions, the efficiency of the computation, etc. Simple models give adequate results for monotonic loading, but models should be able to capture the response of the structure under multiaxial loading conditions, primarily during the failure process. Yield surface, failure surface, and evolution laws are required for this purpose, so plasticity-based models are considered as the most universal solution. Introducing a damage parameter into the plasticity models, the more suitable application is offered. The damage variable covered the cracking and crushing of concrete when the plastic strains occur. The evolution of damage is based on the uniaxial response of the material. The companies and researchers which develop FEM software accepted and implemented many constitutive models for concrete, so it is possible to use the most suitable option according to the selected problem.

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Application of Ceramic Matrix Composite in Automotive Industry

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Glossary

Anisotropic The tendency of a material to exhibit different properties in response to stresses applied along axes in different directions.

Brake A device for arresting or preventing the motion of a mechanism usually by means of friction.

Ceramic-matrix composites (CMC) Materials consisting of a ceramic or carbon fiber surrounded by a ceramic matrix, primarily silicon carbide.

Matrix A material in which the fiber of a composite is imbedded; it can be plastic, metal, ceramic, or glass.

Reinforcement A material added to the matrix to provide the required properties; ranges from short fibers through complex textile forms.

Turbocharger A centrifugal blower driven by exhaust gas turbines and used to supercharge an engine.

Introduction

Composite materials are formed by combining two or more different materials. The basic starting materials have different properties, and their compound gives a whole new material. It has unique, completely new and different properties compared to its constituent components. The goal is to improve the structural, tribological, thermal, chemical or other characteristics of individual materials. The components do not mix or dissolve so that two or more phases are clearly distinguished within the composite.

A composite material is basically composed of:

- (1) Matrix (base) whose content is much higher than other materials and it surrounds and holds together groups of fibers or fragments of reinforcement.
- (2) Filler/reinforcement, whose choice is important for the desired composite properties. They also serve certain additional purposes of heat resistance or conduction, resistance to corrosion and provide rigidity.

Composite constituents can be a variety of materials: non-metals, ceramics, metals, polymers. The properties of the newly formed material will depend on their properties, representation, distribution and bonding. The most common properties of composites are light weight, high stiffness and strength, good damping, corrosion resistance, durability etc. (Vendl, 2012; Stojanovic and Milojevic, 2017; Stojanovic and Glisovic, 2016).

The improved properties of composite materials make it possible to apply them widely. A lot of new ones have been made in recent decades with some extremely useful features. Careful selection of reinforcement and matrix materials and the manufacturing process by which they are formed can provide composites with the properties required for special applications.

Composite materials are divided by type of reinforcement into:

- (1) Particulate-reinforced composites,
- (2) Fiber-reinforced composites,
- (3) Layered composites and
- (4) Structural composites (sandwich structures).

In *particulate-reinforced composites*, hard and brittle particles are distributed as reinforcement and are uniformly distributed through the matrix. Particles can have virtually any shape, size or configuration. The response of a particulate composite can be either anisotropic or isotropic and depend on the particle's size in the composite. Such composites are used for many applications in which strength is not a significant component of the design. It is used to enhance the stiffness of the composites while increasing the strength and the toughness. Because of their mechanical properties, they are used in applications in which wear resistance is required. Furthermore, composites with particulates can be made of various combinations of polymers, metals and ceramics, depending on the ultimate desired properties of the composites.

Fiber-reinforced composites consist of a matrix and reinforcement of mostly fibrous form. They contain fibers of relatively high stiffness and strength that are interconnected by the matrix. Depending on the arrangement of the fibers, the properties of the composites also vary. Different types of fibers, such as glass, carbon or aramid fibers, are used today for composite fibers.

Layered composites or laminar composites consist of multiple layers of reinforcement connected in a matrix. The layers provide the best performance in the load direction, thereby reducing a volume of material and thus reducing weight, which is a major advantage in the automotive and aviation industries (Vendl, 2012). The layers are interconnected by a solid joint. The properties of the composite element depend on the orientation. Laminar composites can be found in many variants, including thin coat materials, thicker coatings, electroplating materials, bimetals, etc. One of the reasons behind the creation of such layered composites is the protection of the surface from the aggressive environment, which is very important for use in the automotive and aviation industries (Kainer, 2006).

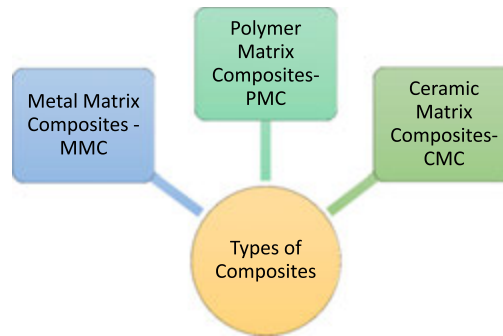


Fig. 1 Types of composites by the matrix material.

Structural composites (sandwich structures) consist of two rigid and solid outer layers connected by the material of small dimensions (the core of the structure). They do not depend on the matrix property, but on the geometric arrangement of the structural elements (Vendl, 2012). The cores of the structural composite are made of various materials such as synthetic rubber, foam polymers, inorganic cements. Frequently used cores are made in the form of a hexagonal cell (honeycomb shape).

Basically, composite material is a combination of two or more constituent materials, often with significantly different chemically and physically properties separated by a distinct interface. The role of the matrix is to keep the reinforcement particles in place and to support them. The base or matrix can be metallic, polymeric and ceramic (Fig. 1). Composite materials are usually classified by the type of material used for the matrix constituent: MMCs – metal matrix composites (matrix is metallic), PMCs – polymer matrix composites (matrix is the polymer) and CMCs – ceramic matrix composites (matrix is ceramic) (Stojanovic, 2013; Vendl et al., 2004; Surappa, 2003; Tucker and Lindsey, 2002).

Depending on the size of the reinforcement, composite materials are divided into the macro-composites, micro-composites and nanocomposites. If the number of reinforcements is two or more, then it is a hybrid composite.

More recently, the preparation of the so-called nanocomposite materials, where at least one phase has nanometer dimensions, is very intensive. The term “nanocomposites” (or “nanostructured materials”) refers to materials whose dimensions of phases (powder particles, structure grains, or layers produced) are in the order of several to one hundred nanometers (Cantor et al., 2004; Tjong, 2009).

In general, metals and polymers are used as matrix materials to achieve the required ductility, while ceramic matrix is further strengthened to improve fracture toughness. For composite materials, thermal stability is largely determined by the type of matrix material. For applications in the highest operating temperature range, materials such as carbon-carbon composites and ceramic composites (CMC) are used (Sitar, 2019).

Ceramics are well known as very hard and rigid materials, resistant to creep at very high temperatures and resistant to a range of aggressive media. The problem of brittleness of ceramic materials is sought to be reduced by the development of modern ceramic composites.

Ceramic Matrix Composites (CMCs) are a subgroup of composite materials consisting of a ceramic matrix combined with various materials (ceramics, graphite, oxides, nitrides, etc.) used as reinforcements designed to improve toughness of conventional ceramics.

The following types of ceramics may be used for matrix material:

- (1) Oxide ceramics: Al_2O_3 , ZrO_2 , SiO_2 , Li and Ca aluminosilicates. The application of oxide fibers in a ceramic mixture can help the final product withstand oxidation, and provide additional strength and reinforcement. Oxide fibers are usually formed through a chemical process, and then heated to finalize the ceramic.
- (2) Non-oxide ceramics: SiC, Si_3N_4 , B_4C , AlN, etc. gives slightly better mechanical properties (high-heat resistance, corrosion resistance, hardness, and oxidation resistance) (Sitar, 2019).

The main advantages of ceramic matrix composites are:

- (1) Stability at extremely high temperatures,
- (2) Good corrosion resistance,
- (3) High hardness,
- (4) Low mass,
- (5) Resistance to temperature shock, etc.

A major disadvantage of CMC is the tendency to brittle break-off.

So far, ceramic composites are very narrowly oriented. For example, CMCs are applied in very specific circumstances where their ability to withstand high temperatures can be used. In ceramic matrix composites, the reinforcing material can be any of the materials both continuous and discontinuous. Ceramics, such as silicon carbide, aluminum oxide, and silicon nitride, can be produced with different fiber diameters, which can then be used to strengthen the composite. Ceramic threads are single crystals with lengths up to 10,000 times their diameter. Threads can have the extremely high-tensile strength, but their length is usually less than 10 mm, making them unsuitable for continuous reinforcement. Ceramic reinforcements are not widely used due to their high cost.

The fracture toughness of these materials is extremely low compared to metals, but lately the fracture toughness has been significantly increased with the development of a new generation of ceramic composites. Particles, fibers or whiskers of one ceramic material are “embedded” in a matrix that is of a different type of ceramic. In this way, the fracture toughness is increased by about 10 times. This improvement in toughness properties is due to the relationship between crack progression and dispersed particle arrangement. The notion of an initial crack refers to the matrix, while cracking propagation is prevented by particles, fibers or whiskers (Sitar, 2019).

The low-density of ceramic composites and thermal conductivity make them attractive for use in heat engines, aircraft, space devices and automobiles when exposed to high temperatures. With cost-effective manufacturing procedures for CMC products, they would be ideal for high-temperature applications under chemically aggressive environments and abrasive wear. These composites are more difficult to manufacture than others because more temperatures and pressures are required, and the ceramic matrix is more difficult to adapt to a polymer or metal reinforcement (Sitar, 2019).

CMC-reinforced with whiskers and particles are prone to catastrophic errors. Continuous fiber-reinforced CMCs are more reliable if the fiber structure carries the load. The reinforcement of Al_2O_3 ceramics with SiC whiskers is tested for tools, turbo-charger parts and valves. CMC is most expected to be applied to gas turbine, rocket and engine parts operating at temperatures above 1600 °C (Djordjevic, 2018).

Ceramic matrix nanocomposites (CMNCs) is used for making nozzle assemblies, materials stoves, systems for converting energy, gas turbines, thermal engines, etc. The ceramic materials are insensitive to extremes of temperature as opposed to the steel at a high temperature changes the mechanical properties. In particular, they showed good composite materials reinforced with carbon fibers, which are very durable at high temperatures, have a high wear resistance, and have substantially lower specific weight compared with steel and aluminum. Carbon fiber reinforced composites are increasingly being used for car parts that are exposed to high loads, such as e.g., brake disks, valves, cylinder liners, spark plugs, sensors, isolators, filters, piston and others. Safe driving is achieved by applying the brake disks made of ceramic composites, because the disks have a great resistance to deformation and wear, thereby enabling a great savings in weight.

Advantages of using the ceramic composite material in the automotive industry are: the ability to create very complex shapes, reduce the cost of after-treatment of parts, the possibility of connecting the parts during the manufacturing process, dimensional stability in extreme working conditions, corrosion resistance, ease of maintenance, longer life time, possibility to work-up and recyclability .

Disadvantages of the CMC application in the automotive industry are: the high production costs, no serial production, lack of skilled labor, stiffness (no deformability), sensitivity to moisture and temperature, inability to repair, toxicity, flammability, etc. Another downside application of ceramic materials is the tendency to fracture, expensive process of production and insufficient research (Velickovic *et al.*, 2018).

Procedures for making ceramic matrix products (García, 2018):

- Hot Pressing

In Hot Pressing technique, pressure and temperature are applied simultaneously. Application of pressure at sintering temperature accelerates the kinetics of densification by increasing the contact stress between matrix particles and particulates/fibers of the dispersed ceramic phase.

- Hot Isostatic Pressing (HIP)

In Hot Isostatic Pressing technique, the ceramic particles of the matrix containing particulates/fibers of the dispersed ceramic phase are contained in a rubber envelope and the pressure is applied by a fluid, isostatically (i.e., has the same magnitude in all directions) along with the temperature simultaneously.

- Sintering from the liquid phase

Liquid phase sintering involves the presence of a viscous liquid at sintering temperatures. The liquid in the narrow channels between the particles (reinforcements) results in a substantial capillary action, which aids in densification (Kim *et al.*, 2017).

Some examples of applications in mechanical engineering are:

- Cutting tools
- Thin layers on metal bases
- Cylinders and valve guides
- Parts of pumps for aggressive media in the chemical industry
- Tools for drawing and guiding wire and pipes
- Rolling and sliding bearings
- Parts of valves exposed to erosion
- Sealing rings
- Filter and heat exchanger parts
- Turbine and engine parts - e.g., turbocharger rotor (Sitar, 2019).

Advanced Composite Materials for Automotive Applications

One of the fastest-growing segments of the composite industry is the land transportation area, with the largest share of the automotive industry. The automotive industry, as one of the most important industries in the world in terms of revenue and number of employees, is a major consumer of composite materials. Nowadays, automotive parts that are not made from composite materials are rare. Composites have been used in the automotive industry since the 1950s. Even then, the benefits of such automotive parts were clear: low mass, cost reduction by combining parts, satisfactory mechanical properties, corrosion resistance, high-temperature resistance, etc. (Milardovic, 2011; Hovorun *et al.*, 2017).

Over the years, the advantages outweighed the disadvantages such as the higher cost of the required ingredients, avoiding new materials, and difficulties in large-scale production. Composites used for less-expensive applications consist of a plastomer or fiberglass matrix filled with glass fibers. Due to the lower price, mineral filler particles are often found in such composites. Driven by high fuel prices and progress in the area of hybrid and electric vehicle, engineers are working hard to drive car development toward a trend where new cars need to be as lightweight as possible while maintaining a high-level of safety. The application of innovative materials leads to the development of projects where the focus is on reducing the mass of the vehicle, while at the same time providing full freedom to designers in the development of the vehicle, its performance and esthetic appearance. New lightweight components that make up composite materials are popular with vehicle manufacturers, especially in the luxury car segment, while guaranteeing complete safety, despite the increasing trend of reducing vehicle mass (Spoljar and Rujnic-Sokele, 2015).

Therefore, composites can now be found in power transmission parts, leaf springs, wheels, turbocharger blades, valves, cylinder liners, catalytic converter liners, particulate filters, spark plugs, fuel detonation sensors, oxygen sensors, and brake disks in sports cars of the mass-produced cars and many more. Emphasis is placed primarily on profit, but also on environmental protection, i.e. ecology; therefore, many studies are being conducted (Milardovic, 2011). Today's contribution of composite materials to automotive technologies extends from driving performance, exhaust gas purification, fuel efficiency improvements, to the esthetic appearance of certain composite parts, making them an indispensable part of the modern automotive industry (Milardovic, 2011; Dolencic, 2018).

In non-aerospace applications of fiber-reinforced glass/glass-ceramic matrix composites, cutting tool inserts, wear-resistant parts, energy-related applications such as heat exchanger tubes, nozzles, exhaust ducts, etc., are the emerging areas. Whisker-reinforced glass-ceramic matrices are expected to find several applications in automotive components, metal forming, cutting tools, etc., due to their low thermal expansion, high thermal shock resistance, high reliability and low material and processing costs (Low, 2006).

Development and Perspective of Ceramic Matrix Composites

The development and availability of thermally stable and corrosion resistant light weight components are a major challenge in modern automotive engineering. The competition in the automotive industry, especially for high-performance luxury and sports cars, demands excellent brake performance, drive comfort and all weather braking ability for new disc brakes. The reinforcement by short, chopped and endless carbon fibers results in fracture toughened ceramic matrix composite (CMC) properties with appropriate friction and reliable mechanical properties in comparison with conventional materials (Gadow and Speicher, 2001; Heinrich and Aldinger, 2001).

The global Ceramic Matrix Composite (CMC) market is \$ 2.2 billion in 2016, \$ 3.3 billion in 2018 with a projected growth rate of 13.74% in the period to 2024. CMC production growth is driven by increasing demand in the automotive, aerospace, military and electronics industries.

Based on market analysis of composite materials with ceramic matrix, oxide, silicon carbide (SiC), carbon and others are used as the matrix material. The increase in the application of CMC, as well as the share of individual materials used to create the CMC matrix, is shown in Fig. 2. Silicon carbide (SiC) with a share of over 25% has the largest market share in 2017 of all above-mentioned materials (Ceramic Matrix Composites (CMC, 2009)).

Based on the analysis of the world market related to ceramic matrix composites, they are most widely used in aviation, defense, automotive, electronics, energy, etc. In 2017, the largest deployment of CMC in the aerospace industry is as much as 35%. After application in the aerospace and defense industries, the largest application of CMC is in the automotive industry (Fig. 3) (Ceramic Matrix Composites (CMCs, 2009)).

Regarding regional application, the largest implementation of CMC is in North America, Asia and Europe, in retrospect.

CMCs are attracting the interests of the aviation and automotive sector thanks to their high power-to-weight ratio, superior mechanical properties and extensive application. Such an increase in interest in CMC materials is expected to shape the future market dynamics of ceramic matrix composites over the forecast period. The increase in fuel prices has triggered the need for lightweight CMC based components to reduce fuel consumption. This results in increased demand for this material in the automotive industry.

Improving vehicle performance in terms of the quality of individual parts as well as reducing emissions is a constant aspiration of the automotive industry. A major driver in the motor vehicle industry is increasing fuel efficiency and reducing vehicle weight. One of the basic ways to achieve these effects is to replace traditional materials with new materials with improved performance, i.e. the use of composite materials. By reducing the mass of the vehicle, a reduction in fuel consumption and consequently, in the emission of harmful gases into the atmosphere is achieved.

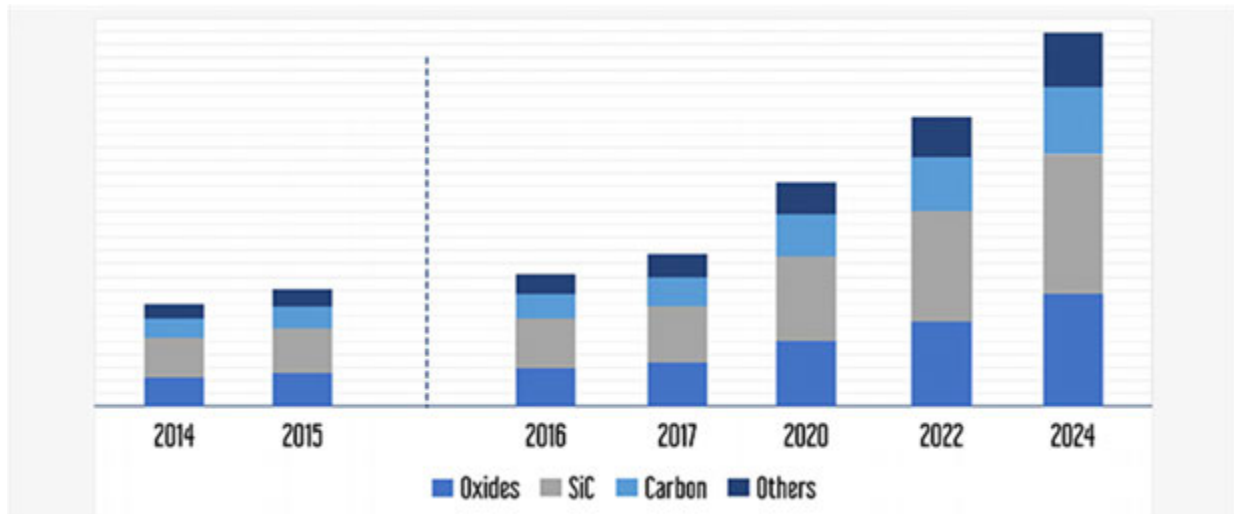


Fig. 2 Ceramic Matrix Composites Market, by product, \$M (2014–2019). Reprinted from Ceramic Matrix Composites (CMC) Market by Product (Oxide, Silicon Carbide, Carbon), By Application (Aerospace, Defense, Energy & Power, Electrical & Electronics), by Geography (U.S., Germany, France, U.K., China, India, Japan) – Global Market Size, Share, Development, Growth, and Demand Forecast, 2014–2024. 2009. Available at: <https://www.psmarketresearch.com/market-analysis/ceramic-matrix-composites-market> (accessed on 25.06.19), with permission.

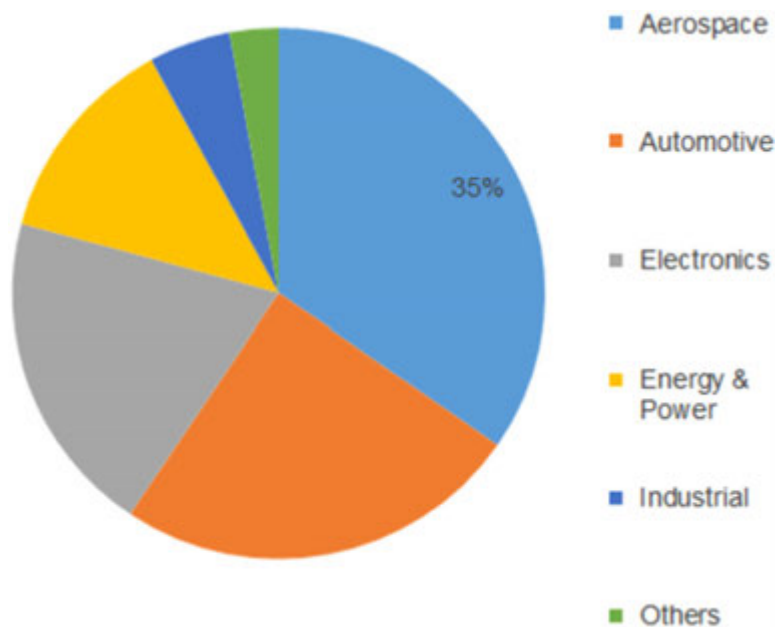


Fig. 3 Global Ceramic Matrix Composites (CMCs) Market Share, by Application, 2017 (%). Reprinted from Ceramic Matrix Composites (CMC) Market by Product (Oxide, Silicon Carbide, Carbon), By Application (Aerospace, Defense, Energy & Power, Electrical & Electronics), by Geography (U.S., Germany, France, U.K., China, India, Japan) – Global Market Size, Share, Development, Growth, and Demand Forecast, 2014–2024. 2009. Available at: <https://www.psmarketresearch.com/market-analysis/ceramic-matrix-composites-market> (accessed on 25.06.19), with permission.

The analysis of the global car market, despite stringent legal regulations, shows a steady increase in the use of composite materials (PMC, MMC and CMC). According to the International Organization of Motor Vehicle Manufacturers, 95 million cars and commercial vehicles were manufactured in 2016. The following diagram by Research (Automotive Composite Market, 2009) U.S. automotive composites' market revenue by product, 2014–2025 (USD Million) is presented in Fig. 4.

Considering the price as well as the weight of the composites, it is evident that the largest is the polymer matrix composite production, followed by the metal matrix composite and finally the ceramic matrix composite.

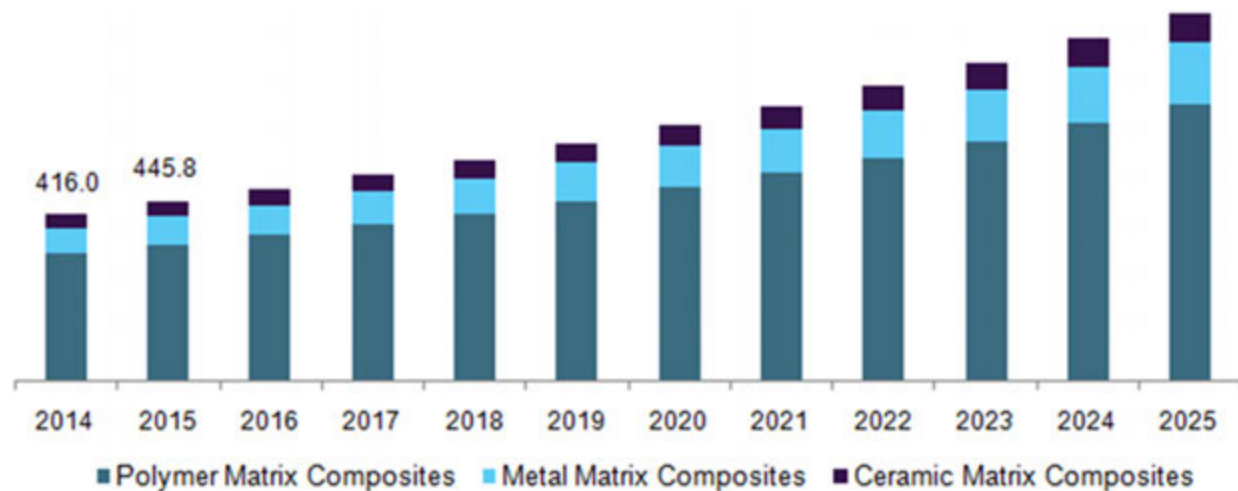


Fig. 4 U.S. automotive composites' market revenue by product, 2014 – 2025. Reprinted from Automotive Composite Market Analysis By Product (Polymer, Metal, Ceramic) By Application (Interior, Exterior, Structural & Powertrain Components), By Region, And Segment Forecasts, 2018 – 2025. 2009. Available at: <https://www.grandviewresearch.com/industry-analysis/automotive-composites-market> (accessed on 29.07.19), with permission.



Fig. 5 Valves in a car engine. Reprinted from Dolencic, F., 2018. Ceramic Matrix Composites in Modern Automotive Industry. Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb (in Croatian). (Bachelor Thesis), with permission.

Ceramic Materials and Components for Engines

Ceramic materials are resistant to oxidation, i.e., generally by fading their properties at elevated temperatures. If they are not prone to brittle fracture, these materials would be ideal for use at high temperatures, as well as for applications where extremely high loads are present, such as e.g. car engine parts. The use of ceramic composites is increasingly common in high-load engine parts that are expected to have high durability at high temperatures, high hardness, or wear resistance, and significantly less specific weight (density) than steel and aluminum (Sitar, 2019; Ma *et al.*, 2017). Current and potential future projects include internal combustion turbodiesel engines, ceramic gas turbines, fuel cells, and electric vehicles as ceramic technologies are intensely involved in the challenge of deploying advanced energy sources.

Important aspects of driving performance are faster driving, instantaneous stopping and cornering stability. These characteristics are directly related to the efficiency of car engines, tires, braking systems and body parts.

Starting from the engine, the ability of the valve system to allow smooth entry and discharge of gases in the combustion chambers is essential to allow the engines to operate at high speeds (Fig. 5). Side valve systems used in the early automotive industry have been converted to more efficient systems and in newer vehicles, Double Overhead Cam (DOHC) with four valves per cylinder have been used. This change was made because the overhead cam allows the valves to open and close



Fig. 6 Compressor mechanical drive - Hellcat 6.2-Liter Supercharged HEMI Engine. Reprinted from Sitar, K., 2019. Application of Composite Materials in the Automotive Industry. Faculty of Mechanical Engineering Varazdin, University North (in Croatian). (Bachelor Thesis), with permission.

smoothly, and the multi-valve system is more efficient for exchanging gases in the combustion chambers due to the large openings (Okada, 2009).

One important aspect is the valve weight reduction, which would also be effective for easier opening and closing. Lightweight materials such as silicon nitride (Si_3N_4) and titanium and aluminum alloys have been considered as possible replacements for nickel-based superalloys currently used for exhaust valves. Recently, titanium and aluminum alloys have actually been used in commercial vehicles, while valves made of silicon nitride have been used in very limited quantities in racing formulas (Okada, 2009; Yamagata, 2005).

Ceramic Matrix Composites (CMCs) For Gas Turbine Applications

Compressor systems enable the development of new generation of extremely high-power engines thanks to the ability to achieve high air pressure in the engine cylinders.

The easiest way to get more power from the engine is to increase the amount of air and fuel that can burn in the engine. One possibility is to increase the volume either by increasing the volume of the cylinders or by adding cylinders. If this is impossible or cost effective, a turbocharger is a simpler and more compact solution.

The purpose of compression is to increase engine power without increasing the working volume and speed. At the constant speed, the power depends only on the mean effective pressure. Increasing the air pressure with the compressor can significantly increase the specific work and engine power. Engine compression causes an increase of the gas pressure in the cylinder, so the higher mechanical load on the engine parts must be taken into account, first the piston mechanism (Jeras, 1992).

There are several types of supercharger:

- Resonant supercharger,
- Mechanical operation of the compressor (Fig. 6),
- Exhaust compressor turbine drive,
- Compex (Compression-Expansion) supercharger (Jeras, 1992).

Propulsion of the gas-turbine compressor is simple, and the exhaust gas energy is used to drive the compressor, which drives the gas turbine. The centrifugal compressor (Fig. 7) and gas turbine are located on a common shaft (Jeras, 1992).

Turbochargers are turbine drives with a forced induction compressor driven by exhaust gas. Turbochargers use a turbine rotor driven by gases from the engine exhaust distributor, and an impeller connected to the turbine common shaft to compress the surrounding air to deliver it to the engine air intake (Kaya, 1999). Turbochargers allow the engine to burn more fuel and air by injecting more fuel and air into the existing engine volume by compaction. Turbochargers are one of the few systems for the additional intake of air into the engine, i.e., they reduce the volume of air entering the engine (Fig. 8). The advantage of reducing the volume of air entering the engine through the intake manifold is that it allows the engine to have more air in the cylinder, and thus more fuel is needed to produce the appropriate mixture. This is why more power is generated from each explosion within each engine cylinder.

A turbocharged engine, by definition, produces more power than a non-turbocharged engine, and this significantly improve the power/mass ratio of the engine (Turbochargers, 2011). This leads to another new trend in the auto industry, which is a downsizing of the engine model itself (Hoffmann, 2009). Engine volume indicates the volume value of a single cylinder multiplied by the number of engine cylinders. The downsizing effect can be seen in the reduction of the number of cylinders and thus the engine capacity,

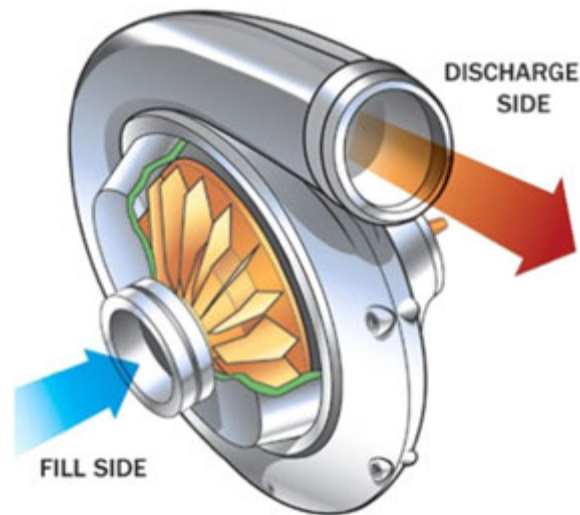


Fig. 7 Centrifugal compressor-Supercharger. Reprinted from Sitar, K., 2019. Application of Composite Materials in the Automotive Industry. Faculty of Mechanical Engineering Varazdin, University North (in Croatian). (Bachelor Thesis), with permission.

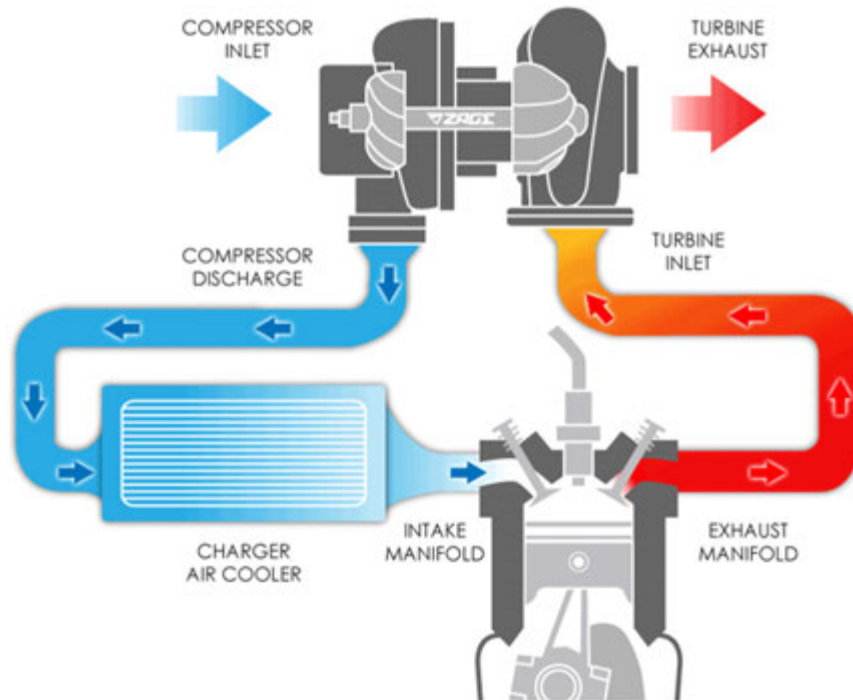


Fig. 8 Turbocharger operating principle. Reprinted from Sitar, K., 2019. Application of Composite Materials in the Automotive Industry. Faculty of Mechanical Engineering Varazdin, University North (in Croatian). (Bachelor Thesis), with permission.

which in turn leads to a reduction in engine mass, less fuel consumption while maintaining or improving the engine performance itself.

Many car manufacturers have already implemented the concept of "downsizing", i.e., Chevrolet has recorded an increase in the sales of more economical four-cylinder units compared to larger six-cylinder and eight-cylinder engines (Hoffmann, 2009).

A significantly lower emission of CO_2 was also observed by applying the concept of "downsizing". Downsizing efficiency can vary up to 5% for diesel engines and up to 40% for gasoline engines (Hoffmann, 2009). The necessary measures to be taken to achieve downsizing efficiency have been considered in the form of compressed air using various turbo-compressors or turbochargers, and thus require modification in the area of material selection of individual parts or re-dimensioning of their geometry and construction. This leads to a comparison and review of the turbocharger and its main parts in terms of the materials of which

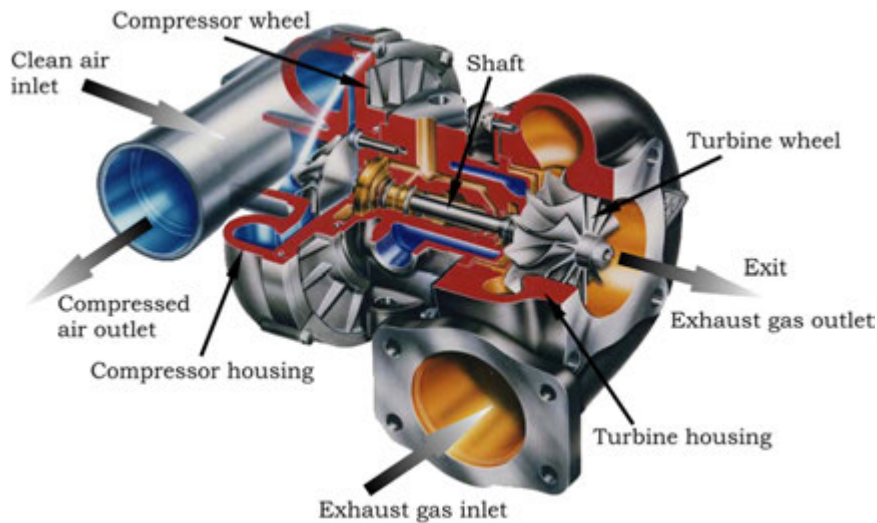


Fig. 9 Turbocharger construction. Reprinted from Dolencic, F., 2018. Ceramic Matrix Composites in Modern Automotive Industry. Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb (in Croatian). (Bachelor Thesis), with permission.

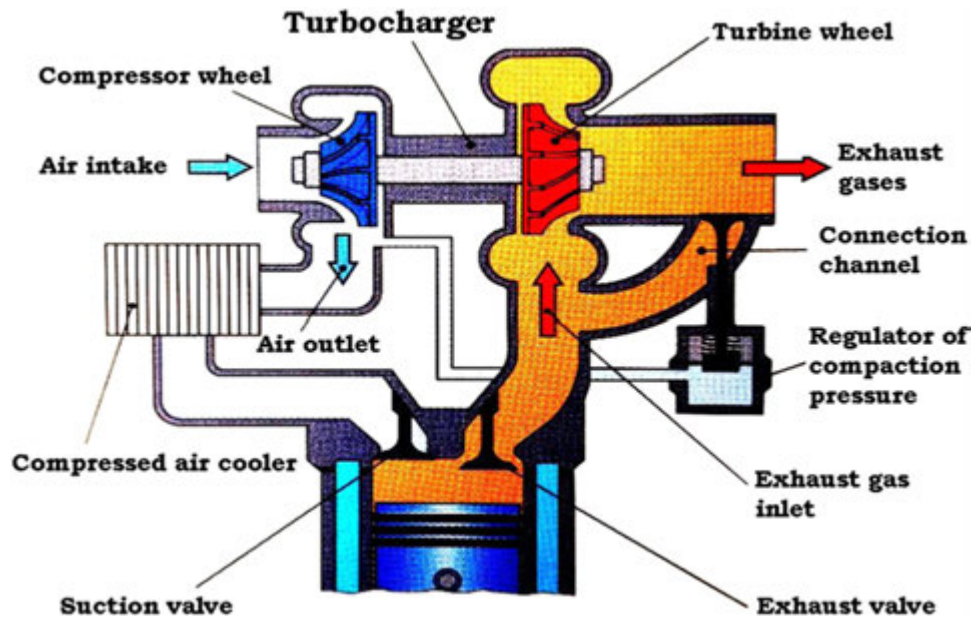


Fig. 10 Schematic illustration of a turbocharged engine. Reprinted from Dolencic, F., 2018. Ceramic Matrix Composites in Modern Automotive Industry. Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb (in Croatian). (Bachelor Thesis), with permission.

they are made of and their properties. For the turbocharger to achieve adequate compression, it uses engine exhaust to spin its turbine, which again accelerates air intake.

The turbocharger is attached to the exhaust manifold of the engine, and these exhaust gases turn the turbine. The turbine is axially connected to a compressor located between the air filter and the engine intake manifold, and that compressor compresses the air that is injected into the cylinders (Fig. 9). The combustion gases from the cylinders pass over the turbine blades that rotate the turbine itself and the more combustion gases pass through the blades, the faster the turbine rotates. On the other side of the shaft to which the turbine is attached, there is a compressor that compresses air into the cylinders. The compressor is so-called a centrifugal pump that draws air into the center of its blades and pushes it further as it rotates (Fig. 10). To maintain 150,000 rpm, the turbine shaft must be attached very carefully. Most of the bearings would probably break at this speed, so the turbochargers use fluid (oil) that is in a very thin layer between the bearing and the shaft, reducing friction while cooling the shaft and other parts of the turbocharger (Turbochargers, 2011).

The turbocharger's turbine typically spins from 100,000 to 150,000 rpm, and as it is directly connected to the engine exhaust, the temperatures at which the turbine operates are very high. During the intake stroke, the turbocharger compresses as much fresh

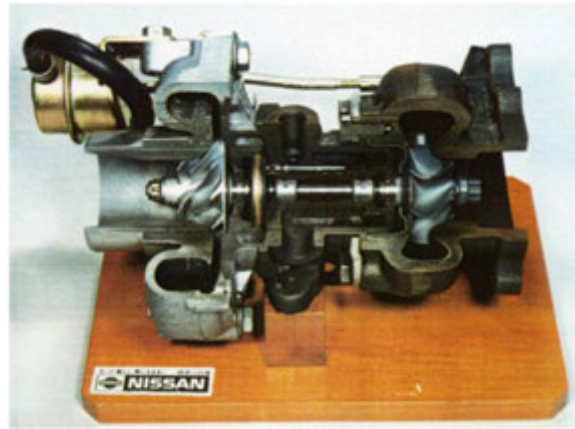


Fig. 11 Nissan silicon nitride ceramic turbocharger. Reprinted from Okada, A., 2009. Ceramic technologies for automotive industry: Current status and perspectives. Materials Science and Engineering B 161, 182–187, with permission.

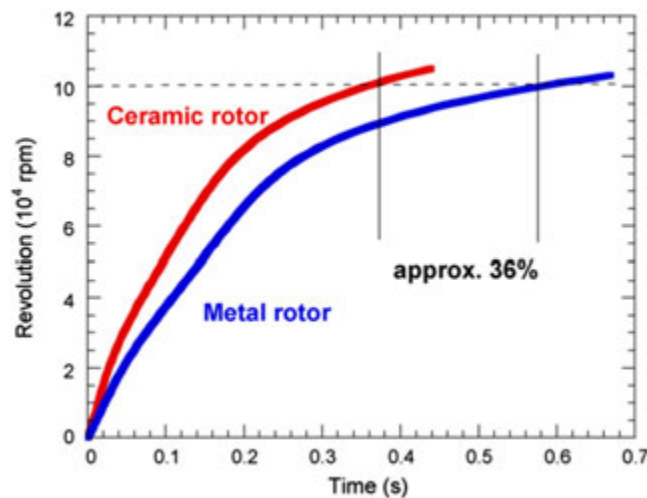


Fig. 12 Comparison of the revolution speed for ceramic and metal turbocharger rotors. Reprinted from Okada, A., 2009. Ceramic technologies for automotive industry: Current status and perspectives. Materials Science and Engineering B 161, 182–187, with permission.

air as possible into the cylinder. In addition, the mixture of fuel and air, i.e., clean air, is partially or completely pre-compressed outside the cylinder (Turbochargers, 2011).

The engine exhaust gases are driven by a turbine wheel and through the shaft by a compressor wheel. The compressor sucks in fresh air and gives it to the cylinders under certain pressure. During pre-compression, the air is heated to 180°C (Fischer *et al.*, 2013). Turbocharger systems are suitable for achieving extremely high power by installing small turbo units to engines. Such chargers act with little delay on the rapid changes in the position of the accelerator pedal because, due to inertia, the exhaust gases cannot accompany the rapid changes in load. This phenomenon is also called “turbo lag” (Fischer *et al.*, 2013).

However, there is an inevitable break between the intention to accelerate which is expressed by pushing the accelerator pedal and the actual acceleration of the car. This lag is caused by the time it takes for the turbine to reach the speed required to reach the pressure of the charger. Reducing the inertial mass of a turbine rotor is an effective way to reduce turbo lag (Kaya, 1999). Fig. 11 shows a ceramic turbocharger made from silicon nitride (Si_3N_4). Turbo lag was reduced in this case due to the fact that silicon nitride is lighter than traditional nickel-based superalloys (Okada, 2009).

The revolution speeds of ceramic and metal turbocharger rotors are compared in Fig. 12. The time required to reach 10,000 rpm of ceramic rotors is reduced by 36% (Okada, 2009).

It should also be noted that turbocharger systems are very suitable for diesel engines, while their application on gasoline engines could result in a detonation phenomenon despite the great advantage in terms of high-output power. In general, gasoline engines require fuel with a specified high anti-detonation index since high-compression engine performance achieves high efficiency. The temperature of the mixture of air and fuel is increased by adiabatic compression and pressure from the turbocharger, and thus these mixtures of gases at high temperatures could lead to self-combustion leading to detonation. The thermal

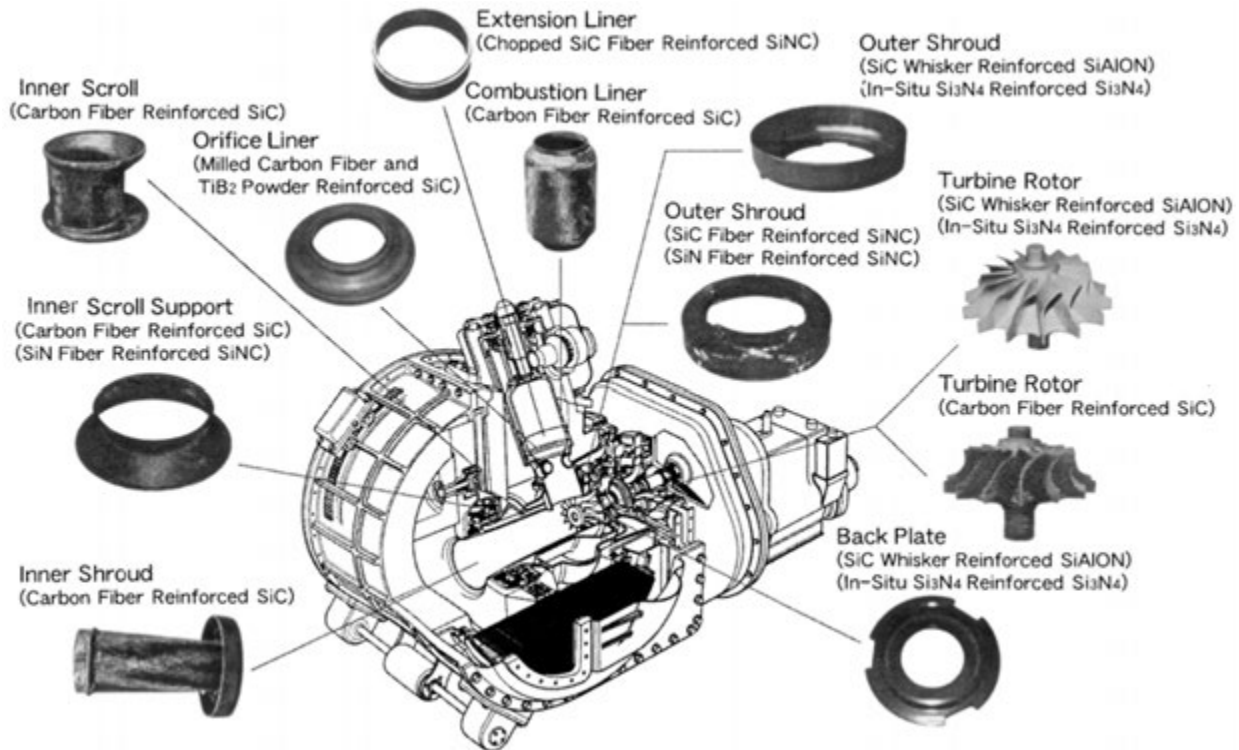


Fig. 13 Ceramic gas turbine components made of ceramic composite material. Reprinted from Kaya, H., 1999. The application of ceramic-matrix composites to the automotive ceramic gas turbine. *Composites Science and Technology* 59, 861–872, with permission.

efficiency of gas turbines is very high for huge engines, but generally low for small engines. It is expected that higher thermal efficiency will only be achieved when small engines operate at higher temperatures (Okada, 2009).

Vehicles equipped with ceramic fuel turbines have been successfully tested under realistic road conditions. However, their performance failed to reach the desired level. The problems identified in the Advanced Fuel Turbines project around 1989 were summarized (Okada, 2009):

- (1) Failure of ceramic rotors caused by foreign objects
- (2) Fuel leaks through ankles
- (3) Thermal deformation
- (4) Insufficient lubrication of rotating parts
- (5) Low strength of ceramic materials at elevated temperatures.

Japan's 100-kW Ceramic Gas Turbine (CGT) Project was launched in 1990 and successfully completed in 1997 (Kaya, 1999). This project was supported by the Ministry of International Trade and Industry and was implemented by the non-profit organization Petroleum Energy Center to achieve goals such as 40% higher thermal efficiency, 100 kW output at 1350°C turbine inlet temperature and the reduction of exhaust gases to adapt to certain eco-standards. Finally, an output power of 92.3 kW and a thermal efficiency of 35.6% were achieved using relatively new materials - ceramic composite materials (Kaya, 1999).

The components of the ceramic gas turbine shown in Fig. 13 consist of a turbine rotor, a back-plate, an orifice liner, an extension liner, an inner scroll support, and other components developed from ceramic composite materials (Kaya, 1999).

Resistance to heat shock, particle collision and creep are essential characteristics required of materials operating at high temperatures. 1 mm diameter zirconium beads were fired into test pieces of various CMCs and monolithic ceramics using a gas gun at high speed to compare the residual strength. Testing of the test specimens, it was concluded that the instantaneous fracture of the turbine rotor caused by the impact of a foreign body caused significant damage to several ceramic components. As shown in Fig. 14, long fiber-reinforced ceramic composites maintain strength even after collision tests at maximum particle velocity. Damage on long fiber-reinforced ceramic composites is limited to only one part of the test body, unlike complete fracture of the material in monolithic ceramics. As explained above, CMC reinforced with long fibers has been confirmed as an extremely resistant material to damage caused by foreign particles (Kaya, 1999).

The application of a turbocharger for compressing engines results in an increased thermal load of the engine parts compared to the engines without compression (Jeras, 1992). Ceramic composites can also be used for their creep resistance characteristics. The silicon-carbide composite reinforced with carbon fibers have a low creep rates of 10^{-9} s⁻¹ at 1700°C and at a load of 200 MPa or more (Fig. 15). It has been confirmed that SiAlON composites reinforced with silicon-carbide whiskers have significantly less

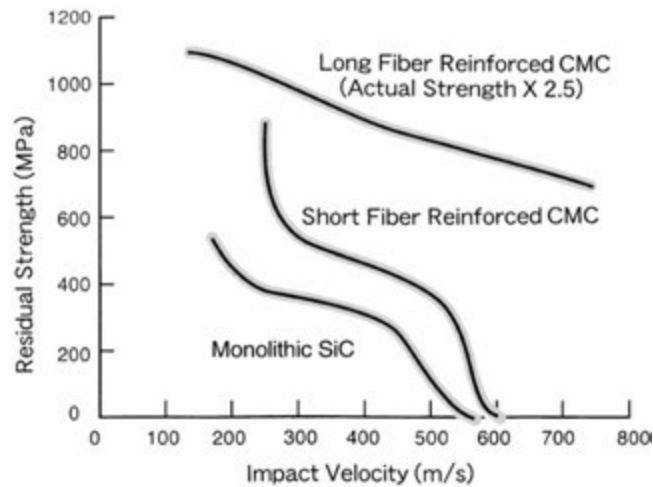


Fig. 14 Residual Strength as a function of particle impact velocity. Reprinted from Kaya, H., 1999. The application of ceramic-matrix composites to the automotive ceramic gas turbine. *Composites Science and Technology* 59, 861–872, with permission.

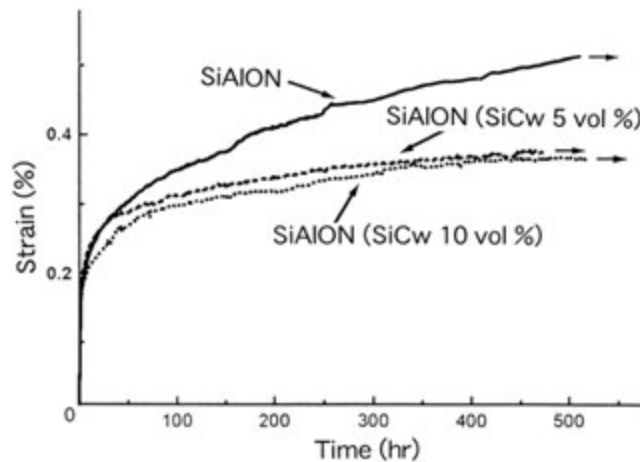


Fig. 15 Creep characteristics of monolithic ceramics and ceramic composite. Reprinted from Kaya, H., 1999. The application of ceramic-matrix composites to the automotive ceramic gas turbine. *Composites Science and Technology* 59, 861–872, with permission.

characteristic deformation at 1200°C and a load of 200 MPa compares to monolithic ceramics even when the amount of whiskers is 10 vol% or less (Kaya, 1999). Such a composite can be sintered without pressure and the composite achieves high flexural strength and high toughness.

After testing, it was found that particle/milled fiber-reinforced ceramic composites have the same or better properties than monolithic ceramics.

It is believed that ceramic composites will be used as an extremely reliable material with thermal and wear resistance after adopting basic processing technologies and the ability to design complex shapes at low cost. In the general case, a long fiber-reinforced ceramic composite has an advantage in various properties over monolithic ceramics, and e.g., shows higher tensile strength and ductility (Fig. 16).

By selecting the orientation and proportion of the reinforcement, the required properties required for a particular product can be modeled. It is expected that new properties that conventional materials do not possess will be assumed by these types of ceramic composite materials due to the above characteristics.

Advanced Friction Systems

During braking, the friction pads press the disks with great force to slow or stop them. As it is necessary to consume the kinetic energy of the vehicle in motion, the same amount of energy on the brakes should be expended on friction. In this way, the disks are warmed up, and their heating increases proportionally with the increase in speed and mass of the vehicle and the frequency of

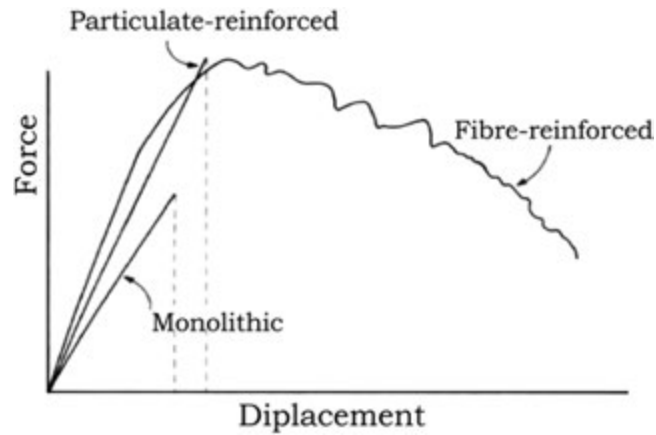


Fig. 16 Schematic force–displacement curves for a monolithic ceramic and CMCs illustrating the greater energy of fracture of the CMCs. Reprinted from Composite Materials. Ceramic Matrix Composites. Muğla Sıtkı Koçman University/Faculty of Engineering. Department of Metallurgical and Materials Engineering. 2009. Available at: <http://www.metalurji.mu.edu.tr/icerik/metalurji.mu.edu.tr/Sayfa/Composite%20Materials7.pdf>, with permission.

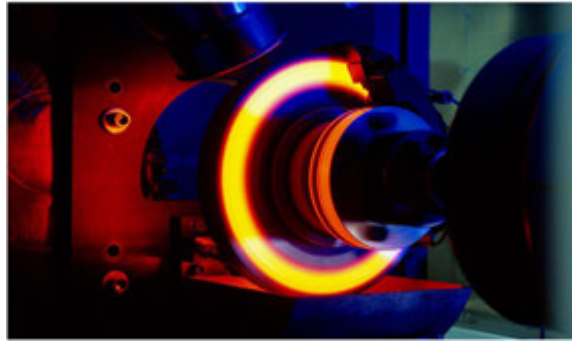


Fig. 17 Brake disc testing. Reprinted from Dolencic, F., 2018. Ceramic Matrix Composites in Modern Automotive Industry. Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb (in Croatian). (Bachelor Thesis), with permission.

braking, which often causes the brakes to overheat and totally fail, **Fig. 17**. Heating causes the material of the disks to dilate and, due to uneven heat distribution through the material, dilation is also uneven. The disc surface becomes uneven over time, which makes the driver feel like vibrations when braking.

The advancement of technology has expanded the use of ceramic composites and is nowadays used in the manufacture of brake disks. In addition to being extremely durable and hard, the ceramic is also very brittle at the same time. Therefore, for the purposes of sports car brake disks it is most commonly used in the form of composite materials, where the silicon carbide matrix is reinforced with carbon fibers (SLR McLaren, 2009).

C/C-SiC composites, made by liquid silicon infiltration (LSI-process), offer superior tribological properties in terms of high coefficients of friction and wear resistance. The carbon fibers lead to an improved damage tolerance in comparison to monolithic SiC, whereas the silicon carbide matrix improves the wear resistance compared to carbon/carbon. C/C-SiC composites are therefore new, outstanding materials for brakes and clutches of high speed cars, trains and emergency brakes.

First attempts to investigate C/C-SiC composites for their use as frictional materials for brake pads and disks started in the early nineties and it shows, in comparison to carbon/carbon, a considerably lower open porosity (less than 5%), a moderately higher density (about 2 g cm^{-3}) and a ceramic share of at least 20% in mass.

Several manufacturers and research institutes are now trying to investigate CMC materials for their use as frictional materials. The resulting materials differ in their constituents (fibers, fillers), microstructure (ceramic content, gradients), properties (density, strength, thermal conductivity) and also in their processing conditions (fiber coating, temperature, etc.). They are all based on carbon fibers and silicon carbide matrices as the main constituents of the composite material. The carbon fibers generally decrease the brittleness of SiC considerably so that the damage tolerance of C/C-SiC components lies in the same order of magnitude as for gray cast iron.

For automotive use, especially for high performance disks the costs of continuous fibers are too high for a serial production with high numbers of items. The most promising way to reduce the costs and to simplify the manufacture is to employ short fiber reinforcements and pressing techniques. The use of short fibers reduces the costs of the raw materials primarily by the reduction of

waste in comparison to bi-directionally woven fabrics. Due to the more isotropic fiber orientation of short fiber reinforced C/C-SiC the thermal conductivity perpendicular to the friction surface of brake disks is generally higher compared to the orthotropic material based on laminated woven fabrics. This leads to lower surface temperatures on the brake disks resulting in an higher and more constant coefficient of friction and lower wear rates (Bansal, 2005).

Since 2009, CMC automotive brake disks are produced and further developed by Brembo SGL Carbon Ceramic Brakes GmbH (BSCCB) a joint venture of Brembo and SGL Brakes, bringing together two of the most experienced experts in brake and CMC technology. Production rate could be increased from several thousand disks in 2002 to about 90,000 disks per annum and about 240 tons per annum in 2011. Hence, production facilities at Brembo in Stezzano (Italy) and at SGL in Meitingen (Germany) are running at almost full capacity. For the manufacture of this safety-critical component, a quality assurance system according to VDA 6.1 and ISO 9001:2000 was introduced, documenting about 600 data from processing and quality testing for every single brake disc (Bansal and Lamon, 2015).

The tribological performance of C-SiC ceramic disks has been studied and it has been found that, with suitable pad compositions, high friction levels can be achieved with very little fade at elevated temperatures leading to reduced vehicle stopping distances from high speed. It is found that a stable tribo-layer is quickly established on the ceramic disc rubbing surface and this seems to consist crucially of iron oxide formed from ferrous ingredients in the brake pad, but hard silica nanoparticles and wear debris from the pad are also constituents of the tribo-layer. The symmetric design of the ceramic rotor (with no “top hat” structure) and the low thermal expansion coefficient mean that there is little thermal deflection (minimal “coning” of the rubbing surface) and no reports of problems of disc thickness variations or judder (Elmarakbi, 2014).

The disks made of a ceramic composite show excellent resistance to thermal expansion and wear, and are still in good condition after 300,000 km. Significant application of ceramic composites is on heavy vehicles, which thanks to such disks can safely brake even at the highest loads. Self-ventilating disks are used for particularly high loads. In rotation, the disc acts as a centrifugal fan, resulting in more efficient cooling, Fig. 18 (Krenkel and Berndt, 2005).

In addition to being able to stand high temperatures, and allowing more intensive braking, ceramic composite disks are also significantly lighter, reducing the moment of inertia. Ceramic composite disks are about 60 times more durable than classic disks and are very expensive. A set of ceramic disks costs more than 3000 euros, which limits their installation on expensive cars. Porsche Ceramic Composite Brake (PCCB) is the most advanced commercially available composite ceramic disc.

Some of the benefits of composite ceramic disks (Dolencic, 2018):

- (1) One of the esthetic advantages of composite ceramic disks is less blackness on the rims, which is especially noticeable on aluminum ones, which also indicates significantly less wear of the disc and pads.
- (2) Overheating during intensive braking is a consequence of temperatures that can rise above 1000°C, without the risk of brake fade.
- (3) Consecutive intensive braking shows the greatest advantages of ceramic disks compared to gray cast iron, because they are more durable, Fig. 19.
- (4) The stopping distance of the brakes at 100 kmh⁻¹ can ideally be reduced to less than 30 m and at 200 kmh⁻¹ below 115 m.
- (5) The braking efficiency of composite ceramic disks changes significantly less depending on temperature, so such brakes are excellent to brake and quite cold.

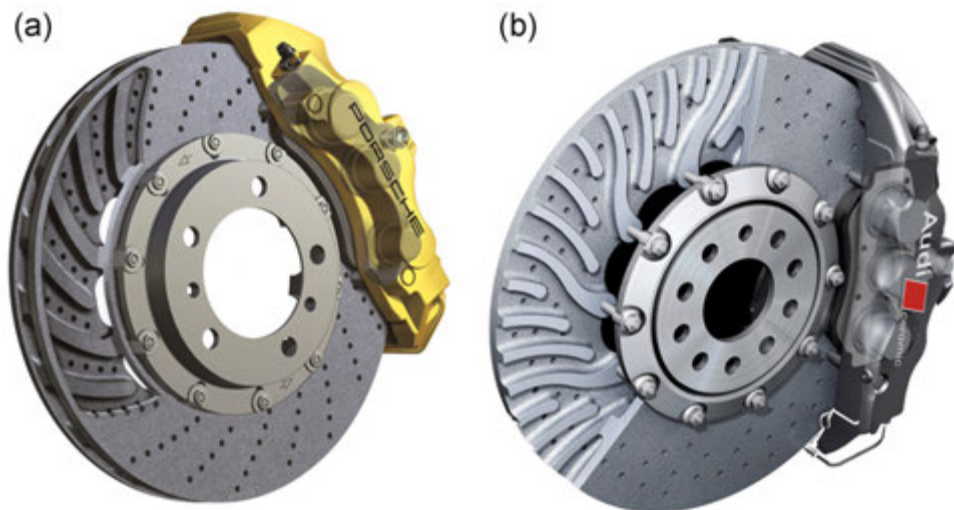


Fig. 18 Self-ventilating ceramic composite disc (a) PCCB-Porsche Ceramic Composite Brake, (b) Audi R8. Reprinted from Krenkel, W., Berndt, F., 2005. C/C-SiC composites for space applications and advanced friction systems. *Materials Science and Engineering* 412 (1–2), 177–181, with permission.



Fig. 19 The ratio of mass of ceramic composite brake disc and gray cast iron disc. Reprinted from Dolencic, F., 2018. Ceramic Matrix Composites in Modern Automotive Industry. Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb (in Croatian). (Bachelor Thesis), with permission.



Fig. 20 C/C-SiC aftermarket tuning brake disks for motorcycles. Reprinted from (See "Relevant Websites section") with permission.

Additionally, CMC brake disks and systems have been developed by AP Racing Ltd., a subsidiary of Brembo SpA, Stilton (Great Britain), MS Production (Slovenia), MOV'IT (Germany), Surface Transforms (Great Britain), and others and are supplied to the tuning aftermarket for selected motorbikes and premium cars such as BMW S1000 RR and Nissan R35 GT-R, respectively, as well as for the use in racing motorbikes (Fig. 20) and cars, especially for rally racing (Bansal and Lamon, 2015).

In another automotive application, C/SiC friction plates have been used in clutches for high-performance, sports and racing cars (Porsche Carrera GT- Fig. 21 and Audi R10 TDI). In all these systems, C/SiC friction plates from BSCCB based on LSI are used. The main advantages of C/SiC friction plates compared to conventional metals and organic or sintermetallic materials are their higher temperature stability and strength, leading to significantly increased torque capacity and energy input and finally to a lightweight and compact design. Compared to C/C, the C/SiC materials offer lower wear, which is favorable for long distance racing series such as the 24 h of Le Mans or the Rally Dakar. In order to minimize mass and volume, continuous fiber reinforced materials based on 2D fabrics are used, leading to high in-plane strength and enabling low wall thicknesses down to 4.5 mm. Compared to a conventional clutch in a Porsche 911, the diameter and weight of the Porsche ceramic composite clutch (PCCC) in the Carrera GT (450 kW, maximum torque > 1000 Nm) could be reduced by 30% from 240 to 169 mm and by 50% from 7.6 to 3.5 kg, respectively (Fig. 22). The small diameter of the clutch enables a low center of gravity for the engine (Bansal and Lamon, 2015).

In comparison to brake applications, clutch disks are more thin-walled and have to withstand mechanical loads resulting from up to 20,000 rpm. Instead of a short fiber reinforcement the ceramic material of the clutch disc is built up with different layers of carbon fiber fabrics to guarantee the necessary strength. The manufacturing is similar to the process of the brake disks: Forming a

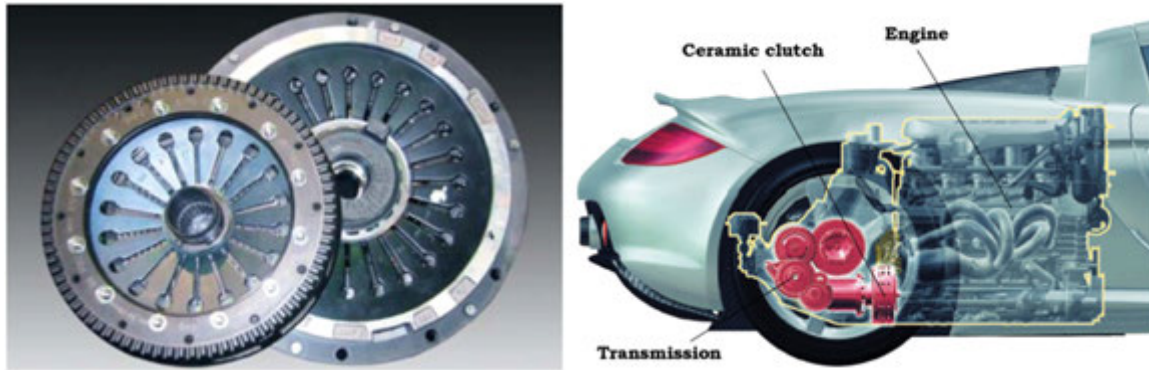


Fig. 21 Porsche ceramic composite coupling (PCCC) in comparison with the conventional clutch. Reprinted from Schröder, S., Walther, J., 2004. The ceramic clutch – a world first from Porsche. Porsche Engineering Magazine, vol. 2 Porsche Engineering Group GmbH. 5–8. Krenkel, W., Berndt, F., 2005. C/C–SiC composites for space applications and advanced friction systems. Materials Science and Engineering 412 (1–2), 177–181, with permission. with permission.



Fig. 22 Ceramic composite clutch from Porsche (PCCC) based on carbon-fiber fabric-reinforced C/SiC. Reprinted from Schröder, S., Walther, J., 2004. The ceramic clutch – a world first from Porsche. Porsche Engineering Magazine vol. 2 Porsche Engineering Group GmbH. 5–8, with permission.

CFRP green body, pyrolysis and siliconizing. Due to the fabric reinforcement a near net shape manufacturing couldn't be realized and flat plates were made. After the siliconizing step the clutch disks are cut out of the resultant ceramic plates with water jet at around 3000 bar (Fig. 23) (Krenkel, 2008).

Based on a detailed analysis, it can be seen that ceramic-based composites are increasingly used for the manufacture of automotive parts and components. The market demands for improving the performance of automobiles are conditioned by the



Fig. 23 Water jet cutting of the clutch disks at about 3000 bar. Reprinted from Schröder, S., Walther, J., 2004. The ceramic clutch – a world first from Porsche. Porsche Engineering Magazine vol. 2 Porsche Engineering Group GmbH. 5–8, with permission.

increasing application of the aforementioned materials. This is especially pronounced for parts exposed to high temperature and extreme pressures. Number of vehicle parts where CMCs replace conventional, i.e. traditional materials are growing year by year. The trend of implementation of CMC in the coming years is very pronounced. The use of oxide, silicon carbide (SiC), carbon and other materials as matrix and reinforcement for CMCs improves their mechanical and tribological characteristics and extends the life of the elements made of them.

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Ion Conducting Materials: Superionic Conductors and Solid-State Ionics[☆]

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Electrical conduction of solid is mostly by electrons or holes as in the case of metals and semiconductors. However, some special types of solids show ionic conduction, the conductivity values of which are often as high as those of aqueous electrolyte solutions. Although, the ionic conduction in solids was already known by Michael Faraday in 19th century (Funke, 2013), it is noticed very useful for applications after 1970: for example, for gas sensors, lithium ion batteries, fuel cells etc. They have been called *solid electrolytes* or *superionic conductors* now; the latter is used especially for those have unusually high ionic conductivity. Faraday found silver ion conduction in Ag₂S, which has also electron conduction together. These materials are now called *Mixed Ionic-Electronic Conductors (MIEC)*, which are inevitable for electrode materials of battery and fuel cell. Growing research on ionic transport in solids and its application after 1970, a technical term of *solid-state ionics* has been established, which refers to the science and technology of ions in motion in solids. International journals of “Solid State Ionics” and “Ionics” have been published, where new materials, applications and fundamental studies have been reported.

Classification of Solids With Ionic Conduction

Ionic conduction in solid was first observed in inorganic crystals like α -AgI, PbF₂ etc., it is now recognized in many varieties of material. Morphologies of ion conducting solids can be classified into crystalline, amorphous (or glassy), and organic polymer materials. Nano-, micro-composite materials are also studied recent years. The ionic species of conduction (mobile ions) also spread from Ag⁺, Cu⁺, F⁻ to include Li⁺, Na⁺, H⁺, O²⁻ etc.; even Mg²⁺ or higher valence cations are also reported mobile in some solids.

Typical ion conducting solids are listed in Tables 1 and 2 with their conductivity and mobile ions. The temperature dependence of conductivity for representative solid electrolytes is shown in Fig. 1.

Fast mobile ions in solids are limited to some monovalent cations like Ag⁺, Cu⁺, Li⁺, Na⁺, and H⁺, which have rather small ion radius comparing to the surrounding anions. Higher valent cations despite their small ion size are so strongly bound to the surrounding anions that it is difficult to move easily in solids. In spite of this, some challenges have been reported on Mg²⁺, Ce²⁺, Sc³⁺ conductors as shown in Table 1.

As anions are, in general, larger in size than cations, their mobility is lower than that of cations. However, comparatively small size anions such as F⁻ and O²⁻ are mobile in some solids. In particular, F⁻ ions in Bi-Pb-In-Sn compounds or glasses are very mobile even near the room temperature. O²⁻ conductors are mostly used at high temperatures above 500°C for sensors or fuel cells. In particular a series of stabilized zirconia is a stable good O²⁻ conductor and is very important for practical uses.

Mechanism of Ionic Conduction in Solids

Fundamental Migration Mechanism of Ions in Solid

There are many types of conduction mechanisms depending on the crystal or non-crystal structure of the solid electrolytes. In a broad way, they are classified into two categories; Type A: sub-lattice liquid type, Type B: point-defect type.

(a) Type A: Sub-lattice liquid type

Most surprising ionic conductors are in this category, whose conductivity is more than 10⁻³ to 10 S cm⁻¹, which is the same order of liquid electrolytes or molten salts. So-called “superionic conductors” are in this category. A typical example is the high temperature phase of silver iodide (α -AgI) which is stable above 147°C to the melting temperature 550°C. The ionic conductivity of α -AgI is 10 S cm⁻¹ at 500°C, which is *higher* than its liquid state. The entropy change ΔS_t of the β - α transition at 147°C is 14.5 JK⁻¹ mol⁻¹ which is larger than the value ΔS_f 11.3 JK⁻¹ mol⁻¹ at the melting temperature of 550°C; this means a half of the component ions (Ag⁺) is fused at β - α transition and the remaining half (I⁻) melts at normal melting point. This is similar to the case of liquid crystal or plastic crystals, which is categorized to a “meso-phase” in between solid and liquid.

Actually, detailed structure analysis of the type A crystals confirmed this concept. In case of the α -AgI, the iodide ions construct a fixed bcc. sublattice, where the silver ions are distributing and migrating randomly among them. A simple picture is shown in Fig. 2, where the two I⁻ locate at the center and the corners of bcc lattice, while the two Ag⁺ are distributing in 42 sites in a unit cell. Moreover, detailed analysis of neutron scattering revealed the silver ions are traveling among these positions very fast like in

[☆]Change History: September 2015. Junichi Kawamura made updates throughout the text and updated the references list of <https://doi.org/10.1016/B0-08-043152-6/00269-2>.

Table 1 Typical ion conducting solids (crystalline solids)

Mobile ion	Composition	Conductivity ($S\text{ cm}^{-1}$)	Note
Ag ⁺	RbAg ₄ I ₅	2.7×10^{-1} (25°C)	
	Ag ₆ I ₄ WO ₄	4.7×10^{-2} (25°C)	
Cu ⁺	7CuBr · C ₆ H ₁₂ N ₄ CH ₂ Br	2.1×10^{-2} (20°C)	
	RbCu ₄ Cl ₃ I ₂	3.4×10^{-1} (25°C)	
H ⁺	H ₃ PW ₁₂ O ₄₀ · 29H ₂ O	2.0×10^{-1} (25°C)	
	CsHSO ₄	8×10^{-3} (160°C)	Superprotonic
	SrCe _{0.95} Yb _{0.05} O _{3-δ}	2×10^{-2} (1000°C)	
Li ⁺	Li ₃ N	3×10^{-3} (25°C)	
	La _{0.25} Li _{0.18} TiO ₃	1×10^{-3} (25°C)	LLT
	Li ₁₄ Zn(GeO ₄) ₄	1.3×10^{-1} (300°C)	LISICON
	Li ₁₀ GeP ₂ S ₁₂	1.2×10^{-3} (25°C)	Thio-LISICON
	Li ₂ (BH ₄)(NH ₂)	2×10^{-4} (25°C)	Hydride
Na ⁺	Na ₂ O · 11Al ₂ O ₃	2×10^{-1} (300°C)	β-Alumina
	Na ₃ Zr ₂ Si ₂ PO ₁₂	3×10^{-1} (300)	NASICON
K ⁺	K ₂ O · 5.2Fe ₂ O ₃ · 0.8ZnO	1.8×10^{-2} (300)	
Mg ²⁺	MgZr ₄ (PO ₄) ₆	3×10^{-3} (800)	
Sc ³⁺	Sc ₂ (WO ₄) ₃	2×10^{-5} (600°C)	
F ⁻	PbF ₂ (+ 2%KF)	2×10^{-2} (200°C)	
	Bi _{0.9} K _{0.1} F _{2.8}	7×10^{-4} (25°C)	
Cl ⁻	PbCl ₂ (+ 3% KCl)	3×10^{-3} (300°C)	
	SnCl ₂	2×10^{-2} (200°C)	
O ²⁻	(ZrO ₂) _{0.9} (Y ₂ O ₃) _{0.1}	2.0×10^{-2} (800°C)	
	(Bi ₂ O ₃) _{0.75} (Y ₂ O ₃) _{0.25}	8×10^{-2} (600°C)	
	La _{0.9} Sr _{0.1} Ga _{0.8} Mg _{0.115} Co _{0.085} O ₃	6×10^{-2} (600°C)	

Table 2 Typical ion conducting solids (glass, glass ceramics, polymer, composite)

Mobile ion	Composition	Conductivity ($S\text{ cm}^{-1}$)	Note
Ag ⁺	60AgI · 40Ag ₂ MoO ₄	2×10^{-2} (25°C)	Glass
	AgI · Al ₂ O ₃ PVA etc.	$10^{-3} \sim 10^{-2}$ (25°C)	Nano-particle
Cu ⁺	50CuI · 50CuPO ₃	1.5×10^{-3} (25°C)	Glass
Li ⁺	37Li ₂ S · 18P ₂ S ₅ · 45LiI	10^{-3} (25°C)	Glass
	50LiI–50Al ₂ O ₃	3×10^{-4} (25°C)	Mesoporous composite
	PEO · LiClO ₄	1×10^{-5} (25°C)	Polymer
	Li ₂ O–Al ₂ O ₃ –TiO ₂ –P ₂ O ₅	1.3×10^{-3} (25°C)	Glass ceramics
H ⁺	ZrO ₂ –3(PO _{2.5}) + xH ₂ O	1×10^{-2} (25°C)	Sol–gel glass
F ⁻	(InF ₃) _{0.35} (SnF ₂) _{0.2} (PbF ₂) _{0.35}	8×10^{-4} (150°C)	Glass

Abbreviation: PEO, polyethylene oxide.

liquid. Thus, the type A ionic conductor can be regarded as a meso-phase between liquid and solid. Similar sublattice liquid state is observed in fluoride structured F⁻ conductor PbF₂, whose conductivity is also 1 S cm^{-1} at 900K as shown in Fig. 3. It is regarded as a superionic phase like α-AgI, although the transition to the superionic state is a continuous second order type (Faraday transition), which is different from first order transition of β to α-AgI (Catlow, 1989).

α-AgI or PbF₂ is an example of three dimensional (3D) ionic conductor, where the mobile ions can move any directions through the 3D conduction channels. 2D and 1D ionic conductors are also known. A typical example is sodium ion conduction in Na β-alumina (Na₂O · 11Al₂O₃), which has a layered structure as shown in Fig. 4. The crystal framework is formed by spinel block layers composed of aluminum and oxygen. Na⁺ ions (large gray circles) are distributing in a plane between the two spinel layers which are supported by the pillars of oxygen (double circles).

The array of Na⁺ ions in the plane is ideally ortho-triangle, however the midpoint between oxygen-pillars (called *mid-oxygen site*; small circles in Fig. 5) are also energetically available. Therefore, Na⁺ ions can easily move from their normal sites to the mid-oxygen sites and vice versa, which give rise to the liquid-like high Na⁺ ion conduction. In comparison to the above mentioned AgI or PbF₂ which have 1st or 2nd order phase transitions to low temperature insulator phases, Na β-alumina shows no clear phase transition even below 10K, whose conductivity decreases linearly in Arrhenius plot; so that some authors (Boyce and Huberman, 1979) categorize AgI as type I, PbF₂ to type II and Naβ-alumina to type III.

One dimensional or quasi-1D ionic conduction is often found in tunnel structured compounds. An example is a ramsdellite-type Li₂TiO₃, in which Li⁺ ions migrate through a tunnel surrounded by octahedra and tetrahedra of TiO_n. Some hollandite-type

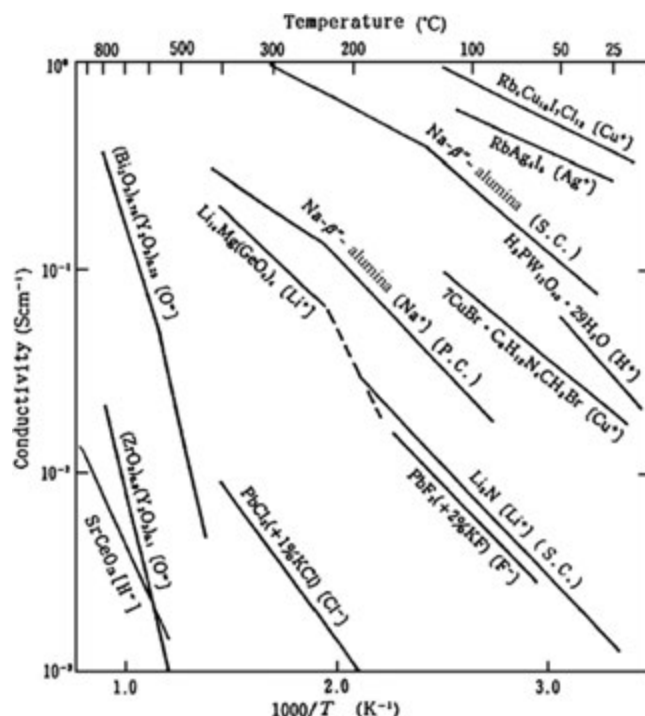


Fig. 1 Conductivity of ion conducting solids. S.C. single crystals, P.C. poly crystal.

crystals as $K_{2x}Mg_xTi_{8-x}O_{16}$ has also one dimensional tunnels surrounded by TiO_n . The potassium ions K^+ are distributing and moving freely in the tunnels, which give rise to the very high conductivity of 10 S cm^{-1} at microwave frequency. However, the conductivity at low frequency or dc region becomes very low probably due to some blocking impurities or defects in the tunnels.

When the tunnels of different directions are connected with each other, the macroscopic ionic conduction becomes 3D. The *Na superionic conductor* (NASICON) family represented as $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($x < 2$) is a typical example (see Section Sodium Ion Conductors).

It is necessary to mention briefly the structure and conduction mechanism of amorphous ionic conductors such as AgI- Ag_2MoO_4 glass or solid polymer electrolytes as PEO-LiClO₄ shown in [Table 2](#) (Junichi Kawamura *et al.*, 2006). Although these materials have no long-range order like crystals, they have some short ($\sim 1 \text{ nm}$) and intermediate ($\sim 10 \text{ nm}$) range orders. In case of AgI- Ag_2MoO_4 glass, the glass is locally composed of AgI₄ and MoO_4 units connected randomly. The silver ions are mainly moving through the AgI rich regions like in the α -AgI, which link to form random conduction channels. In lower temperatures, some silver ions are trapped by the oxide ions resulting to the decrease in conductivity. No thermodynamic phase transition is seen, but the glass transitions are observed between the melt and the superionic glass as well as between the superionic glass and insulator glass. In case of the polymer electrolyte as PEO-LiClO₄, the lithium ion is trapped in a cage made of coordinating four oxygens in polyethyleneoxide network, whose micro Brownian motion allows the lithium ion to migrate from one cage to the other like transferring an apple through many baskets by bucket brigade manner.

(b) Type B: Point-defect type

Any ionic crystal has in principle some extent of ionic conductivity due to the intrinsic lattice defects in the crystal. Typical examples are so called Frenkel and Schottky defects created by the thermal energy at a temperature. Frenkel defect is a pair of *interstitial* cation M_i and cation *vacancy* V'_M , whereas the Schottky defect is a pair of cation vacancy V'_M and anion vacancy V'_x as shown in [Fig. 6](#).

Number density of the defects n can be expressed by defect equilibrium; for example, in case of Frenkel defects as,

$$n(T) = \sqrt{NN'} \exp\left(\frac{-G_F}{2kT}\right) \quad (1)$$

where N and N' are the number of normal sites and interstitial sites respectively. ΔG_F is the formation free energy of a Frenkel defect pair, k is the Boltzmann constant, T is the absolute temperature. Thus, the intrinsic defect density is determined by the defect formation free energy ΔG_F . On the other hand, extrinsic defects can be artificially created by heterovalent doping, for example, the doping of $MgCl_2$ to $NaCl$ creates sodium vacancy V'_{Na} . The concentration of the extrinsic defects can be calculated by defect equilibrium theory (Kroger, 1964).

Once some defects are created in a crystal, they can migrate rather easily in the solid. There are fundamentally three ways of ionic transport by lattice defects; (1) vacancy mechanism, (2) interstitial mechanism, and (3) interstitialcy mechanism which are illustrated schematically in [Fig. 7](#).

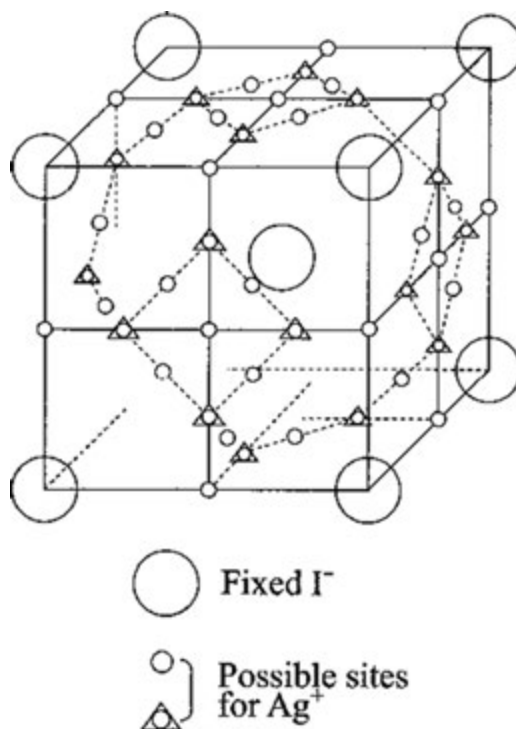


Fig. 2 Stock model of α -AgI structure.

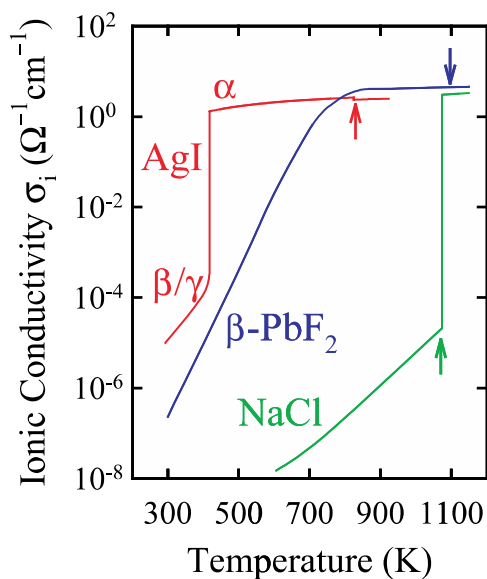


Fig. 3 Ionic conductivity of AgI, PbF₂ and NaCl, from Hull, 2004.

Small cations can migrate by both interstitial and vacancy mechanisms, although the large anions diffuse mostly by anion vacancy process. A typical example is the oxide-ionic conduction in stabilized zirconias such as $(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$ (see Section Oxide Ion Conductors), where an O^{2-} ion hops from its normal site to an adjacent anion vacancy V_{O} leaving a new vacancy behind. Another example is the fluoride-ionic conduction in fluorite-type solid solutions composed of $\text{Ca}_{1-x}\text{Na}_x\text{F}_{2-x}$ ($x \leq 0.05$), in which a monovalent sodium replaces a divalent calcium in CaF_2 to create a fluoride ion vacancy. In these materials, the vacant sites of movable ions are rather limited, for example, in the above described stabilized zirconia the number of oxide-ion vacancies is only 5% of normal anion sites. Thus, the ionic conductivity of the defect type solid is not so high as that of type 1 superionic conductors.

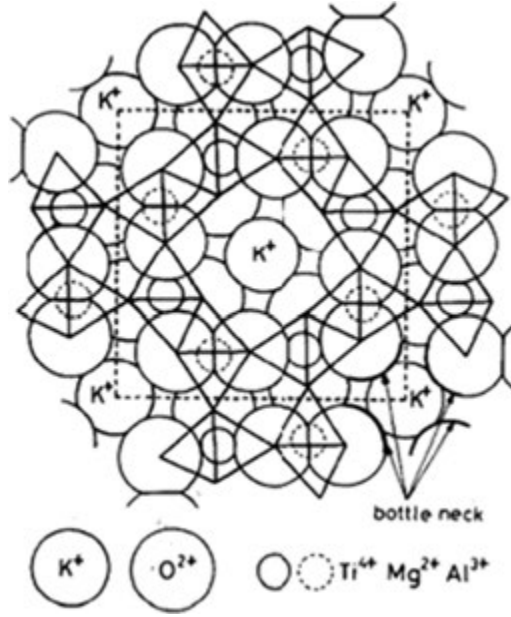


Fig. 4 Structure of Hollandite type one dimensional K^+ conductor (Yoshikado *et al.*, 1982).

Theory of Ionic Conduction in Solids

When the carrier density n is known, the ionic conductivity σ can be estimated by the following Nernst formula as,

$$\sigma = zen\mu \quad (2)$$

where μ is the mobility of the mobile ions; z and e represent their ionic valence and elementary charge, respectively. In case of Type A superionic conductors, the carrier density n is equal to the total mobile ions; for example, all Ag^+ in α -AgI. In the case of Type B defect type solid, n is the number of the mobile defects expressed like Eq. (1). For vacancy mechanism, the charge carriers are regarded as vacancies instead of mobile ions themselves, thus the n should be the number of the vacancies.

The mobility μ in Eq. (2) is related to the diffusion coefficient D of the mobile ion by,

$$\mu = zeD/kT \quad (3)$$

Thus the ionic conductivity σ is expressed as the following Nernst-Einstein equation:

$$\sigma = (ze)^2 nD/kT \quad (4)$$

The diffusion coefficient of an ion in solid is well described by "jump model"; a mobile ion located in a bottom of a potential well with thermal vibration $(v)_0$ attempt frequency overcomes a potential barrier ΔG_m in order to move to another site as shown in Fig. 7. Then the transition rate $(v)(T)$ is expressed as,

$$(v)(T) = (v)_0 \exp\left(\frac{-\Delta G_m}{kT}\right) \quad (5)$$

and the diffusion coefficient D is expressed as,

$$D = \frac{1}{6}(v)a^2 \quad (6)$$

where a is the jump distance shown in Fig. 7.

Thus, the ionic conductivity is expressed as,

$$\sigma(T) = \frac{(z_i e)^2 a^2 (v)_0}{kT} n_i \exp\left(\frac{-\Delta G_m}{kT}\right) \quad (7)$$

In case of Type A superionic conductors, since the n_i is almost independent of temperature the slope of $\log \sigma T$ vs. $1/T$, which is usually called *activation energy* gives the estimation of the barrier height.

On the other hand, in case of Type B defect type ionic conductors, the n_i strongly depends on the temperature as given in Eq. (1) for intrinsic Frenkel defect case. In this case the ionic conductivity is expressed as,

$$\sigma(T) = \frac{(z_i e)^2 a^2 (v)_0}{kT} \sqrt{NN'} \exp\left(\frac{-\Delta G_m + \Delta G_F/2}{kT}\right) \quad (8)$$

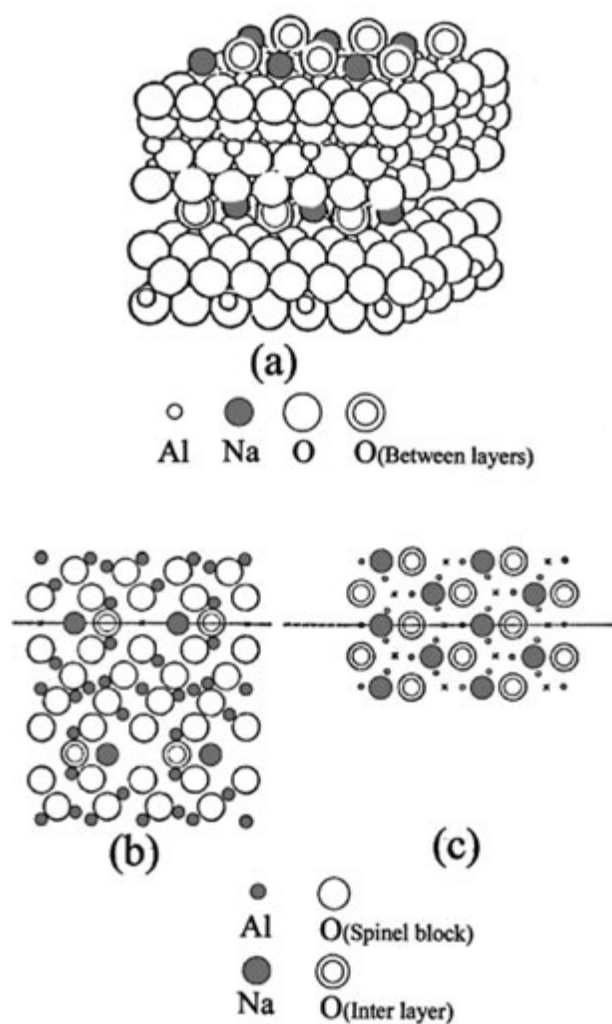


Fig. 5 Layer structure of β alumina. (a) Outward appearance, (b) cross-sectional plane perpendicular to layer, (c) arrangement of Na^+ between layers.

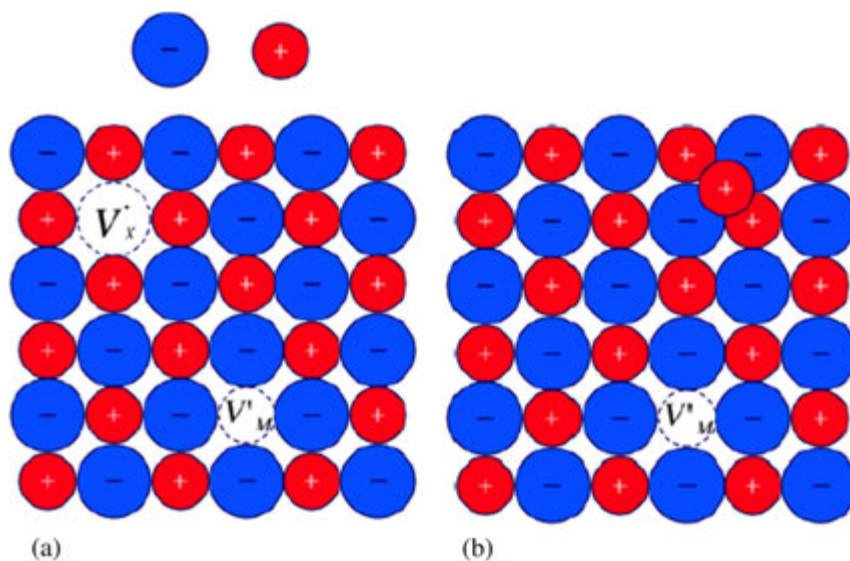


Fig. 6 Schematic model of (a) Schottky defect and (b) Frenkel defect.

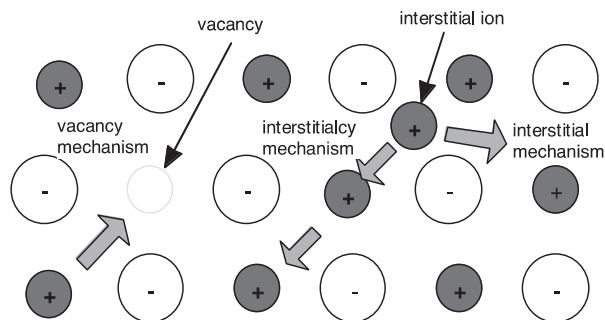


Fig. 7 Typical ion transport mechanisms in point defect type ionic conductor; (1) vacancy mechanism, (2) interstitial mechanism and (3) interstitialcy mechanism.

So, the apparent activation energy gives the sum of the defect formation and migration energies. The estimation of these energy values is a key subject of the solid state ionics, which are tabulated in some literatures (Kroger, 1964). One can say, the Type A superionic conductor is a limit of Type B with negligible value of ΔG_f .

It is worthwhile to compare the diffusion coefficient D_σ from conductivity experiment with the values from other experiments such as a tracer diffusion coefficient D_{Tr} by radio isotope experiment, or pulse-field gradient NMR technique D_{NMR} etc. An example is given in Table 3, where the value estimated from the conductivity by Eq. (4) is expressed by D_σ . Fairly good agreement is seen between D_{comp} and D_{Tr} , however small difference is also seen. The ratio of them is called Haven ratio HR or correlation factor f , which is an index of many-body effect and/or backward correlations of mobile ions.

The diffusion phenomenon that changes the chemical composition of the solid is called *chemical diffusion* and its coefficient is named the *chemical diffusion coefficient* (D_{chem}). In mixed conductors (see Section Mixed Ionic-Electronic Conductors) such as $Ag_{2+\delta}S$ the diffusion of Ag^+ from the outside is accompanied by the diffusion of excess electrons changing the composition of the solid. The D_{chem} value of $Ag_{2+\delta}S$ at 200°C is evaluated to 0.1–0.3 cm² s⁻¹ and that of $Ag_{2+\delta}S$ is 0.5–1.5 cm² s⁻¹ depending on the composition. The chemical diffusion coefficient is now very useful to analyze electrode reactions in lithium ion batteries, SOFC etc.

Typical Examples of Ionic Conductor

Silver and Copper Ion Conductors

As is already explained in Sections Classification of Solids With Ionic Conduction and Mechanism of Ionic Conduction in Solids, the best-known example is α -AgI, which has a sublattice melting superionic conductor state above 147°C; below this temperature, it transforms into a β (wurtzite) or γ (zincblend) phase of poor conductivity as shown in Fig. 2. Many attempts have been made to stabilize the high conductivity α -AgI phase down to the lower temperatures, for example, by substituting other cations M for silver or substituting other anions X for iodide ions. Table 4 shows some room temperature-type silver ion conductors thus synthesized. Of these, $RbAg_4I_5$ has the highest conductivity of 2.7×10^{-1} S cm⁻¹ at room temperature.

Similar to α -AgI, the high temperature crystal form of CuI is an average structure with high Cu^+ conductivity. Similar attempts were made to stabilize the superionic phase to room temperature. Copper ion conductors thus synthesized are listed in Table 1.

Among these, $Rb_4Cu_{16}Cl_{13}I_7$ exhibits the highest conductivity, 4.7×10^{-1} S cm⁻¹ at room temperature; this value is the highest one not only among the Cu^+ -conductors but also among all kind of solid electrolytes ever known.

Some other attempts have been made to stabilize the high temperature superionic phase to room temperature; (1) by glass formation with other oxides etc., (2) confined nano-size structures. For the glass formation, for example, the melt of AgI and some oxides as Ag_2MoO_4 are quenched to room temperature, whose ionic conductivity is about 10^{-3} S cm⁻¹. The confined nano-size crystals are made by various techniques such as mechanical milling, sol-gel synthesis, or after annealing of glassy materials etc., whose ionic conductivity is around $10^{-4} \sim 10^{-3}$ S cm⁻¹, as shown in Table 2.

Sodium Ion Conductors

A well-known sodium ion conducting solid is so called Na β -alumina, the chemical composition of which is typically expressed as $Na_2O_{11}Al_2O_3$. The crystal has a layer structure and the incorporated sodium ions can migrate along the layer as shown in Fig. 5 in Section Mechanism of Ionic Conduction in Solids. β'' -alumina which is represented as $Na_2O \cdot 4 \sim 6 Al_2O_3 \cdot xMO_n$ also have a layer structure and the sodium ion conductivity of these materials is higher than that of Na β -alumina. Other cations such as Ag^+ , K^+ , Li^+ , Sr^{2+} , Ba^{2+} and Eu^{2+} can be fully substituted for sodium ions in Na β -alumina and the resultant ceramics show electrical conduction due to the migration of those ions. Na β'' -alumina is used as a solid electrolyte for sodium-sulfur batteries (NaS batteries) for large-scale energy storage systems (see Section NaS battery). Another typical sodium ion conductor is a series of NASICON, the chemical composition of which is represented as $Na_{1+x}Zr_xSi_{3-x}O_{12}$ ($x < 2$). In this type of oxide, sodium ions are surrounded by a 3D network of SiO_4 tetrahedra and ZrO_6 or PO_6 octahedra which share corners, and the sodium ions are mobile

Table 3 Diffusion coefficients D_σ and D_{Tr} for several solid electrolytes

Material	Mobile ion	Temperature ($^{\circ}\text{C}$)	D_σ ($\text{cm}^2 \text{s}^{-1}$)	D_{Tr} ($\text{cm}^2 \text{s}^{-1}$)
$(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$	O^{2-}	1000	4.2×10^{-8}	4.2×10^{-8}
$\alpha\text{-AgI}$	Ag^+	200	2.53×10^{-5}	1.76×10^{-5}
$\alpha\text{-RbAg}_4\text{I}_5$	Ag^+	25	3.68×10^{-5}	1.75×10^{-5}
Sodium β -alumina	Na^+	25	6.8×10^{-7}	4.0×10^{-7}
Potassium β -alumina	K^+	25	3.17×10^{-9}	9.6×10^{-10}
Silver β -alumina	Ag^+	25	3.1×10^{-7}	1.7×10^{-7}
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$	H^+	27	4.5×10^{-6}	

Abbreviations: D_{comp} , component diffusion coefficient; D_{Tr} , tracer diffusion coefficient.

Table 4 Typical sodium ion conductors

Mobile ion	Composition	Conductivity (25°C) (S cm^{-1})	Note
Na^+	$\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$	2×10^{-1} (300°C)	Na β -Alumina
	$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$	3×10^{-1} (300°C)	NASICON
	$\text{Na}_2\text{O}-\text{R}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$	2×10^{-2} (300°C)	Narpsio (R=rare earth)
	Na_3PS_4	2×10^{-4} (25°C)	
	$\text{Na}_2\text{B}_{10}\text{H}_{10}$	10^{-2} (110°C)	Hydride

through the channel of the network structure. Glass ceramics called Narpsio of $\text{Na}_2\text{O}-\text{R}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ (R=rare earth), which consist of a skeleton structure of $12(\text{SiO}_4)^{4-}$ tetrahedra-membered rings exhibit high Na^+ conductivity up to $10^{-1} \text{ S cm}^{-1}$ at 300°C and has good biocompatibility. Hollandite type 1D conductor $\text{Na}_x\text{Ti}_{2-x}\text{Ga}_{4+x}\text{O}_{11}$ has very high Na^+ conductivity only at high frequency (see Section Fundamental Migration Mechanism of Ions in Solid). Most of work have been done on oxide materials, however some new types of sodium ion conductors are developed; for example, as a sulfide of a cubic Na_3PS_4 is found to show $2 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C and is used for an all solid state sodium battery (Hayashi *et al.*, 2012). A very new group of ionic conductors based on boron hydrides as $\text{Na}_2\text{B}_{10}\text{H}_{10}$ is discovered to show $10^{-2} \text{ S cm}^{-1}$ at 110°C , which has a unique icosahedral dodecahydro-closo-dodecaborate ($\text{B}_{12}\text{H}_{11}^{2-}$) anions (Udovic *et al.*, 2014; Table 4).

Lithium Ion Conductors

Recent advancement of lithium ion batteries strongly demands lithium ion conductors both for active materials for electrodes and electrolytes. As for the solid electrolytes, lithium ion conductivity of $10^{-3} \text{ S cm}^{-1}$ is now achieved by sulfide based materials; for example, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ shows $1.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C (Fig. 8; Kamaya *et al.*, 2011), and some glassy or partially crystalline glasses have the same order (Fig. 8). Lithium nitride Li_3N has also $10^{-3} \text{ S cm}^{-1}$ at room temperature. Unfortunately, however these materials are unstable under open air.

Since oxide materials are known rather stable under open atmosphere, many efforts have been devoted to find new materials with high lithium ion conductivity. The conductivity of $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ (named LISICON) is about $1 \times 10^{-2} \text{ S cm}^{-1}$ at 200°C and that of $\alpha\text{-Li}_2\text{SO}_4$ is extremely high ($\sim 1 \text{ S cm}^{-1}$) above 573°C . Li β -alumina prepared by ion-exchange from Na β alumina shows $10^{-3} \text{ S cm}^{-1}$ at 25°C . $\text{La}_{0.51}\text{Li}_{0.34}\text{TiO}_{2.94}$, which is a perovskite-type oxide based on $\text{La}_{2/3}\text{TiO}_3$ has high conductivity at room temperature. Glass ceramics composed of $\text{Li}_{1.55}\text{Ti}_{1.75}\text{Al}_{0.25}\text{Si}_{0.3}\text{P}_{2.7}\text{O}_{12}$ with a NASICON-type crystalline phase has $1.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C , which is called "OHARA glass" and is commercially available. Although those oxides are stable in open air, they are reduced by a contact with lithium metal, which hampers the application to lithium battery. Some Garnet-type structured compounds as $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$, $\text{Li}_6\text{Ba-La}_2\text{Ta}_2\text{O}_{12}$ and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) are found stable to the contact to lithium metal and has a reasonable conductivity of $10^{-4} \text{ S cm}^{-1}$ at room temperature, which can be used for all-solid state lithium batteries (Venkataraman Thangadurai *et al.*, 2004). For the application to thin film batteries, rather low conductivity glasses such as Li_3PO_4 ($\sim 10^{-6} \text{ S cm}^{-1}$ at 25°C) or its oxynitride called LIPON can be used for the electrolyte; they are stable to both lithium metal anode as well as high voltage cathodes.

An interesting new class of lithium ion conductors have been developed in hydride series starting from LiBH_4 . LiBH_4 has a lithium ion conductivity of $10^{-2} \text{ S cm}^{-1}$ above 117°C , and its derivative of $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$ shows $2 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature (Motoaki Matsuo *et al.*, 2009). These hydrides are stable to lithium metal, although they react with oxide cathodes.

In relation to the lithium ion battery, a great advance has been achieved in organic or organic-inorganic hybrid ion conductors, where polymer, gel, ionic liquid and plastic solids are included. In particular, organic polymers or gel electrolytes are used as the electrolyte for lithium ion batteries. The details of the organic-inorganic hybrid ion conductors are out of this column; some of them are listed in Tables 2 and 5 (MacFarlane and Forsyth, 2001; Junichi Kawamura *et al.*, 2006, 2007). The highest conductivity of the polymer electrolytes is around $10^{-4} \text{ S cm}^{-1}$ at room temperature although the transference number of the lithium is less than 0.5 and the counter anion is much higher.

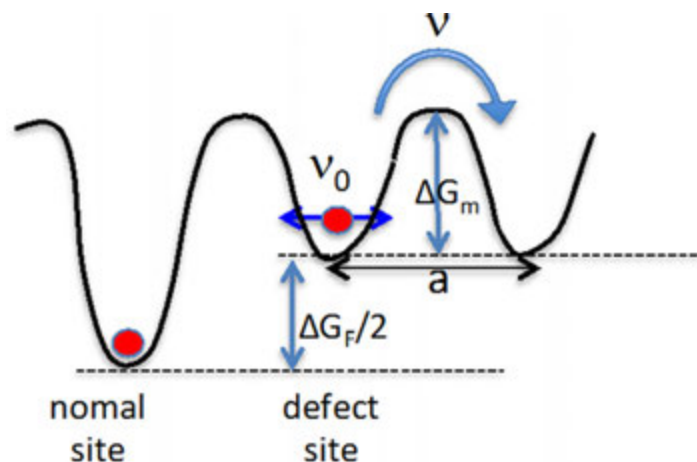


Fig. 8 Jump model of ion migration in solids.

Proton (or Hydride Ion) Conductors

A good proton-conducting solid would be a promising material for future hydrogen energy systems. They will be of use as a solid electrolyte for fuel cells, hydrogen production, hydrogen separation, hydrogen sensors, and membrane reactors. Various kinds of proton conducting solids have been synthesized. They are roughly classified into six categories as represented in Table 6 with typical compounds belonging to each category. Hydrated heteropoly acids such as $\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$ and $\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$ show very high protonic conductivity at room temperature. However, they are unstable at elevated temperatures even below 100°C to lose the water molecules to decrease in their conductivity. The conductivity of CsHSO_4 , which is an anhydrous compound, increases at 144°C due to transformation of its crystal structure. Some related materials as $\text{M}_3\text{H}(\text{XO}_4)_2$ ($\text{M}=\text{Rb}, \text{Cs}, \text{NH}_4$; $\text{X}=\text{S}, \text{Se}$) or phosphates have been known to show high proton conductivity up to $10^{-2} \text{ S cm}^{-1}$ at around 200°C “superprotonic” state. A typical structure of the superprotonic state is shown in Fig. 9 for CsH_2PO_4 , where the PO_4 is rotating very fast to promote the proton jump between the two oxygens.

The charge carriers in H_3O^+ - β'' -alumina and NH_4^+ - β'' -alumina are considered to be partly protons and partly hydronium or NH_4^+ must be replaced for Na^+ by ion exchange of conventional Na- β'' alumina. It is known that the mobility of protons in H_xWO_3 and H_xMoO_3 is very high. But the conductivity itself cannot be measured since electronic conduction in these oxides is much higher than that of protons.

Organic polymers based on polyethyleneoxide or polyvinylalcohol with inorganic acid shows proton conduction, the conductivities of which are the order of $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature.

Development of proton conducting ceramics which are stable over a wide range of temperature has been desired because they are very useful materials for electrochemical energy conversion and sensors (see Section Sensors). Some doped perovskite-type oxide solid solutions based on SrCeO_3 and BaCeO_3 are known to exhibit appreciable protonic conduction under a hydrogen-containing atmosphere at elevated temperatures. $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ and $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ belong to this class of proton conductors. These ceramics exhibit only p type electronic conduction in the atmosphere free from water vapor or hydrogen. However, when water vapor or hydrogen is introduced into the atmosphere at high temperature, electronic conductivity decreases and protonic conduction occurs rapidly. When the SrCeO_3 based ceramics are exposed to hydrogen gas at high temperature, they become almost pure protonic conductors, the conductivity of which is about $1 \times 10^{-2} \text{ S cm}^{-1}$ at 900°C (somewhat lower than that of YSZ shown in Fig. 1). Since zirconate-based ceramic $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\delta}$ exhibits proton conduction and their mechanical strength as well as chemical stability is better than those of cerates, they are used as a solid electrolyte for hydrogen sensors (see Section Sensors) although its conductivity is rather low.

It is necessary to add some recent reports on hydride ion conductors. The existence and possible transport of hydride ion (H^-) in some oxides are reported in $12\text{CaO}-7\text{Al}_2\text{O}_3$ (Hayashi *et al.*, 2002), $\text{BaTiO}_{2.4}\text{H}_{0.6}$ (Yoji Kobayashi *et al.*, 2012), La_2LiHO_3 etc. (Kobayashi *et al.*, 2016; $\sigma = 10^{-6} \text{ S cm}^{-1}$ at 500K), in which the observed ionic conductivity is reported not due to the proton (H^+) conduction but by hydride ion (H^-). The size of the H^- ion is about $1.2 \text{ \AA}$, which is suitable for ionic conduction. Although some critical discussions are still going (Norby *et al.*, 2004), these materials might open a new frontier of ionics field (Table 7).

Other Cation Conductors

Some other cations are conducting in solids, although their conductivity is rather low; for example, potassium ions K^+ can move in the tunnel-structured oxide $\text{K}_2\text{O}_{5.2}\text{Fe}_2\text{O}_{30.8}\text{ZnO}$. Divalent cation conductors $\text{M}^{(\text{II})}\text{Zr}_4(\text{PO}_4)_6$ are known, where $\text{M}^{(\text{II})}$ is Mg^{2+} , Zn^{2+} , Mn^{2+} etc.; for example, $\text{MgZr}_4(\text{PO}_4)_6$ has the Mg^{2+} ion conductivity of $3.4 \times 10^{-3} \text{ S cm}^{-1}$ at 800°C (Nomura *et al.*, 1992). As was shown in the previous sections, β - and β'' alumina are capable to allow many kinds of cations to migrate in its conduction planes; for example, Ba^{2+} , Cd^{2+} , Sr^{2+} , Eu^{2+} , most of which are prepared by exchanging Na^+ ions with those ions. Trivalent

Table 5 Typical lithium ion conductors

Mobile ion	Composition	Conductivity (25°C) ($S\text{ cm}^{-1}$)	Note
Li^+	Li_3N	3×10^{-3}	
	$\text{La}_{0.25}\text{Li}_{0.18}\text{TiO}_3$	1×10^{-3}	LLT
	$\text{Li}_{2+2x}\text{Zn}_{1-x}(\text{GeO}_4)_4$	2×10^{-6}	LISICON
	$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	1.2×10^{-3}	Thio-LISICON
	$\text{Li}_2(\text{BH}_4)(\text{NH}_2)$	2×10^{-4}	Hydride
	$\text{Li}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$	10^{-3}	Li- β -Alumina
	$\text{Li}_{1.55}\text{Ti}_{1.75}\text{Al}_{0.25}\text{Si}_{0.3}\text{P}_{2.7}\text{O}_{12}$	1.2×10^{-3}	OHARA glass
	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$	10^{-4}	LLZ
	$\text{Li}_3\text{PO}_3.9\text{Nb}_{0.17}$	2×10^{-6}	LIPON
	$\text{Li}_{3-2x}(\text{In}_{1-x}\text{M}_x)_2(\text{PO}_4)_3$	10^{-5}	
	$37\text{Li}_2\text{S} \cdot 18\text{P}_2\text{S}_5 \cdot 45\text{LiI}$	10^{-3}	Glass
	$50\text{LiI}-50\text{Al}_2\text{O}_3$	3×10^{-4}	Mesoporous composite
	$\text{PEO} \cdot \text{LiClO}_4$	10^{-5}	Polymer

Table 6 Typical solid proton conductors

Category and material	Conductivity ($S\text{ cm}^{-1}$)	Note
<i>Hydrate compounds</i>		
$\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$	2×10^{-1} (25°C)	Room temperature type. Unstable at dry atmosphere
$\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$	2×10^{-1} (25°C)	
$\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$	4×10^{-3} (20°C)	Unstable above 100°C
$\text{HClO}_4 \cdot \text{H}_2\text{O}$	3×10^{-4} (27°C)	
$\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$	3×10^{-4} (25°C)	
<i>Anhydrous compounds</i>		
$\text{C}_6\text{H}_{12}\text{N}_2(\text{H}_2\text{SO}_4)_{1.5}$	2×10^{-4} (200°C)	Stable below 200°C
$\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$	1×10^{-4} (160°C)	
CsHSO_4	27×10^{-3} (147°C)	
KOH	2×10^{-3} (350°C)	mp. 406°C
<i>β-alumina type oxides</i>		
$\text{H}_3\text{O}^{+}\text{-}\beta\text{-Al}_2\text{O}_3$	1×10^{-4} (25°C)	Prepared by ion exchange method
$\text{NH}_4^{+}\text{-H}_3\text{O}^{+}\text{-}\beta''\text{-Al}_2\text{O}_3$	1×10^{-4} (25°C)	
$\text{NH}_4^{+}\text{-}\beta/\beta''\text{-Ga}_2\text{O}_3$	1×10^{-2} (200°C)	
<i>H-insertion compounds</i>		
HxWO_3		W-bronze structure. High electronic conduction. With protons in motion
HxMoO_3		
<i>Oxides with lattice defects</i>		
$(\text{ThO}_2)_{0.85}(\text{Y}_2\text{O}_3)_{0.15}$	6×10^{-3} (1200°C)	Perovskite-type structure Protonic conduction under H-containing atmosphere
$\text{La}_{0.96}\text{Ca}_{0.04}\text{YO}_{3-\alpha}$	5×10^{-4} (1000°C)	
$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$	1×10^{-2} (900°C)	
$\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-\alpha}$	2×10^{-2} (800°C)	
<i>Organic polymers-inorganic acids</i>		
$\text{PEO-H}_2\text{SO}_4$	2×10^{-4} (25°C)	Polyethylene oxide
$\text{PVA-H}_3\text{PO}_4$	$1 \times 10^{-5} \sim 1 \times 10^{-3}$ (25°C)	

cations of Sc^{3+} and Al^{3+} were reported mobile in $\text{Sc}(\text{WO}_4)_3$ and $\text{Al}(\text{WO}_4)_3$ respectively, although their conductivities are rather low 10^{-5} S cm^{-1} at 600°C (see Table 1).

Fluoride and Chrollide Ion Conductors

As a fluoride anion is monovalent and the smallest in its size among different kinds of anions, it is expected to be mobile in solids. Fluorite (CaF_2) is a typical fluorite-type structure of f.c.c. and the array of anions is somewhat coarse. As already shown in Fig. 1, the fluoride ion conductivity of PbF_2 is $3 \times 10^{-6}\text{ S cm}^{-1}$ at 600K and increases up to 10^{-4} S cm^{-1} at 800°C, where some (5~10%) fluoride anions distribute in interstitial sites and generate fluoride ion vacancies which cause the high fluoride ion conductivity at high temperature.

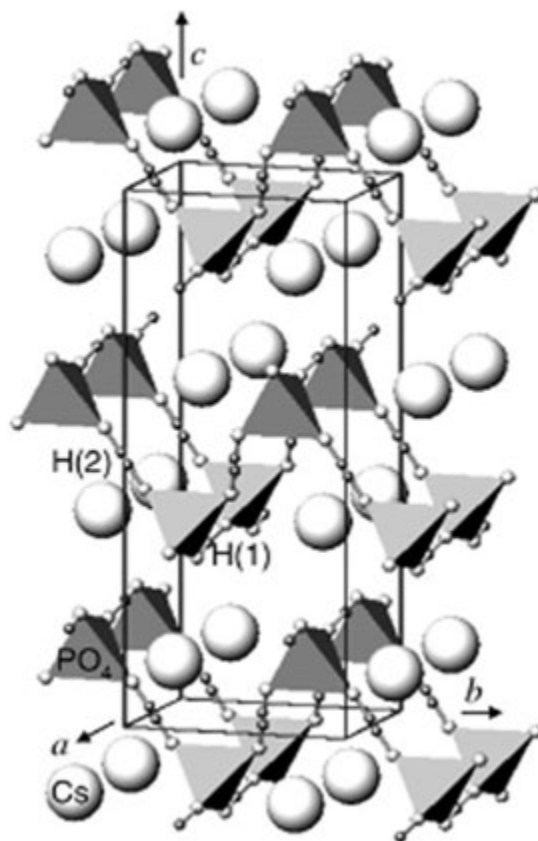


Fig. 9 Structure model of CsH_2PO_4 (from Haile *et al.*, 2007).

A doping of lower valent cations for calcium sites creates anion vacancies, which allows fluoride anions to migrate in the crystal. The solid solution $(\text{CaF}_2)_{0.95}(\text{NaF})_{0.05}$ is an example. In fact, there are many kinds of fluoride ion conductors. They are roughly classified into three categories, ie, fluorite-type, PbCl_2 -type, and tysonite-type. Among the fluoride ion conductors, PbSnF_4 , whose crystal structure is a fluorite-related type, shows the highest conductivity as shown in Fig. 10. Since the tysonite-type LaF_3 is chemically stable with moderate conductivity, it is used as a selective electrode for fluoride ion sensors. Some fluoride glasses as $(\text{InF}_3)_{0.35}(\text{SnF}_2)_{0.4}(\text{PbF}_2)_{0.35}$ has also high conductivity around $10^{-3} \text{ S cm}^{-1}$ at 150°C . Typical fluoride conductors are listed in Table 8.

As chloride ions are larger in size than fluoride ions, oxide ions and most of cations of the metallic elements, it is difficult for them to migrate easily in solids. However, some chloride ion conductors are known although their conductivity is low; for example, $(\text{PbCl}_2)_{0.97}(\text{KCl})_{0.33}$ shows $3 \times 10^{-3} \text{ S cm}^{-1}$ at 300°C . Doped SnCl_2 shows also high chloride conductivity but is chemically unstable in the atmosphere. It has been reported that the perovskite-type chloride CsPbCl_3 exhibits chloride ion conduction of $1 \times 10^{-3} \text{ S cm}^{-1}$ at 500°C .

Oxide Ion Conductors

Similar to the fluoride ion conductors, rather small size oxide anion O^{2-} is often mobile in some solid oxides at elevated temperatures. Many kinds of oxide-ion conductors are known and are classified into several types (Tables 9 and 10). A series of defect fluorite-type oxides which have an appreciable amount of oxide ion vacancy is the most familiar. The host oxides are tetravalent oxides MO_2 or trivalent oxides (sesqui-oxides) M_2O_3 ; typical example of the former is stabilized zirconia, in which trivalent or divalent cations are partially substituted for tetravalent zirconium in ZrO_2 . Thus, oxide ion vacancies are formed as a result of charge compensation as shown in Fig. 11. At elevated temperatures of several hundred degree Celsius, oxide ions can easily move with the help of the vacancies and give rise to the high oxide ion conductivity. A representative ceramic is yttria-stabilized zirconia (YSZ), the typical composition of which is $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ (8Y). This ceramic is very popular and widely used in many fields because the conductivity is fairly good and cheap in cost. Magnesium-doped zirconia is often used because of its good resistance to thermal shock and calcium-doped zirconia because of low cost, although the conductivity is not as high as that of YSZ.

Ceria-based solid solutions composed of $(\text{CeO}_2)_{1-x}(\text{M}_2\text{O}_3)_x$ are also oxide ion conductors of this class and the conductivity is, in general, higher than that of zirconias, although they are not so strong against a reducing atmosphere at high temperature as

Table 7 Typical solid proton and hydride ion conductors

Material	Conductivity ($S\text{ cm}^{-1}$)	Note
$\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$	2×10^{-1} (25°C)	Unstable at dry atmosphere
$\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$	2×10^{-1} (25°C)	Unstable above 100°C
$\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$	4×10^{-3} (20°C)	
$\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$	3×10^{-2} (25°C)	
$\text{C}_6\text{H}_{12}\text{N}_2(\text{H}_2\text{SO}_4)_{1.5}$	2×10^{-4} (200°C)	Stable below 200°C
$\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$	1×10^{-4} (160°C)	
CsHSO_4	2.7×10^{-3} (147°C) I	
KOH	2×10^{-3} (350°C)	
$\text{H}_3\text{O}^+ \cdot \beta\text{-Al}_2\text{O}_3$	1×10^{-4} (25°C)	Prepared by ion exchange method
$\text{NH}_4^+ \cdot \beta\text{-}\beta''\text{-Ga}_2\text{O}_3$	1×10^{-2} (200°C)	
H_xWO_3		Mixed conductor
H_xMoO_3		
$(\text{ThO}_2)_{0.85}(\text{Y}_2\text{O}_3)_{0.15}$	6×10^{-3} (1200°C)	Perovskite-type structure
$\text{La}_{0.96}\text{Ca}_{0.04}\text{YO}_{3-x}$	5×10^{-4} (1000°C)	Protonic conduction under H-containing atmosphere
$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$	1×10^{-2} (900°C)	
$\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-x}$	2×10^{-2} (800°C)	
$\text{PEO-H}_2\text{SO}_4$	2×10^{-4} (25°C)	Polyethylene oxide
$\text{PVA-H}_3\text{PO}_4$	$1 \times 10^{-5} \sim 10^{-3}$ (25°C)	Polyvinyl alcohol
La_2LiHO_3	1×10^{-6} (237°C)	Hydride ion conductor?

zirconia. The solid solutions based on thorium such as $(\text{ThO}_2)_{0.9}(\text{CaO})_{0.1}$ are oxide ion conductors although they are accompanied by hole conduction under an oxidizing atmosphere.

The conductivity of pure $\alpha\text{-Bi}_2\text{O}_3$ (below 730°C) is low and electronic. However, it is transformed above 730°C to $\delta\text{-Bi}_2\text{O}_3$ which belongs to the defect fluorite-type structure and this phase exhibits very high oxide ion conductivity as shown in Fig. 12. This high conductivity phase can be stabilized by substituting tri-, penta-, or hexavalent cations partially for bismuth; for example, $(\text{Bi}_2\text{O}_3)_{0.73}(\text{Y}_2\text{O}_3)_{0.27}$, $(\text{Bi}_2\text{O}_3)_{0.85}(\text{Nb}_2\text{O}_5)_{0.15}$, and $(\text{Bi}_2\text{O}_3)_{0.75}(\text{WO}_3)_{0.25}$, which exhibit high conductivity at around 500°C . However, they are not available for practical use since they are easily reduced under a reducing atmosphere at elevated temperatures. $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$.

Another category of oxide ion conductors is a series of *perovskite-type oxides* which have oxide ion vacancies in their lattice. The oxide ion vacancies are created by partial substitution of lower valent cations for host cations. One example is $\text{CaTi}_{0.7}\text{Al}_{0.3}\text{O}_{2.85}$ in which the tetravalent titanium in CaTiO_3 is partially replaced by trivalent aluminum to create oxygen vacancies, whose conductivity is as high as that of calcia-stabilized zirconia although it contains some electronic conduction under an oxidizing atmosphere at high temperature. Among the perovskite-type oxides, the LaGaO_3 -based oxides such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_3$ have very high oxide ion conductivity at around 600°C where next generation SOFC is expected to operate (see Section Applications of Ion Conducting Solids). The high-temperature phase (above 950°C) of brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$ is also a typical example, in which one sixth of the oxygen in the normal perovskite structure is deficient. This high conductivity phase can be stabilized by substituting cerium or zirconium partially for indium. Scheelite-type oxides such as PbWO_4 have been reported to exhibit oxide ion conduction with moderate conductivity.

Mixed Ionic-Electronic Conductors

The charge carrier in a solid electrolyte is typically one kind of ions of which the solid is composed. Stabilized zirconia, Na β -alumina and RbAg_4I_5 under normal condition are regarded as pure ionic conductors of oxide ions, sodium ions, and silver ions, respectively. However, some solids show both ionic and electronic conduction and sometimes the electronic conductivity σ_e is much higher than the ionic conductivity σ_i although the ionic conductivity itself is markedly high. These solids are called *mixed ionic-electronic conductors* (MIEC) or simply *mixed conductors*. The mixed conduction is often attributed to a nonstoichiometry of the compound especially in case of ionic crystals as oxides, sulfides and halides, where not only ionic defects but also electronic defects such as excess electrons e^- or holes h^+ can be generated by the nonstoichiometry. However, it is worth noted that even in a metallic solid like LiIn alloy, the lithium (ion) is fast diffusing, which can be categorized in MIEC also.

Silver chalcogenides such as $\text{Ag}_{1+\delta}\text{S}$ and $\text{Ag}_{1+\delta}\text{Se}$ seem outwardly to be n type electronic conductors. However, Ag^+ ion conductivity of these solids at elevated temperatures ($> 200^\circ\text{C}$) is in the order of 1 S cm^{-1} which is comparable to that of $\alpha\text{-AgI}$ at the same temperature range. The electronic conductivity is a few orders of magnitudes higher than the ionic one depending on the composition. Cu_2S is another example of a chalcogenide mixed conductor. This material shows Cu^+ ion conduction as well as p type electronic (hole) conduction.

Some insertion compounds can be put into this category; for example, Li_xCoO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, Li_xTiS_2 , etc., are known as the cathode materials for lithium ion batteries, which have both electronic (hole) and lithium ionic conductivities. Also, in the anode (negative electrode) materials as Li_xC and alloys as Li_xIn , Li_xSn , Li_xSi , Li_xAl , Li_xMg , etc., are thought of electronic and lithium ion

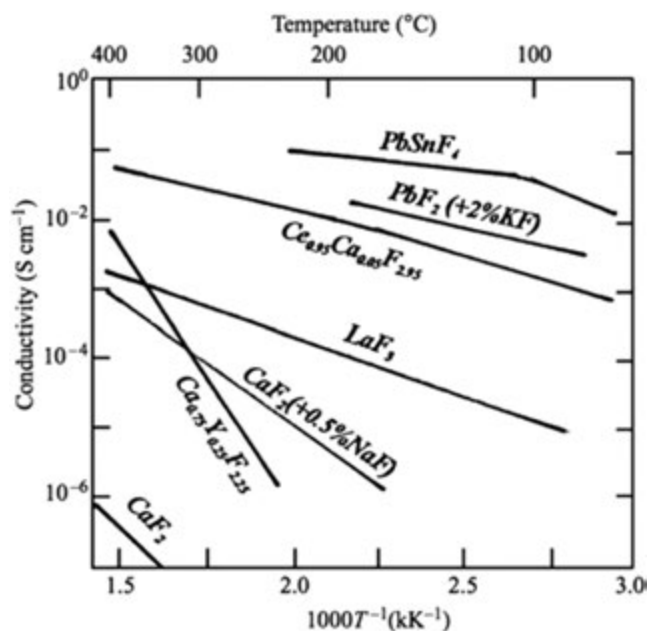


Fig. 10 Conductivity of fluoride ion conductors.

Table 8 Typical fluoride ion conductors

Material	Conductivity ($S\text{ cm}^{-1}$)	Note
$\text{Ca}_{0.894}\text{U}_{0.091}\text{Ce}_{0.005}\text{F}_{2.187}$	8×10^{-3} (150°C)	Fluoride
$\text{Pb}_{0.45}\text{Bi}_{0.25}\text{F}_{2.25}$	6×10^{-3} (150°C)	
PbSnF_4	8×10^{-2} (150°C)	
$\text{Ce}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$	6×10^{-3} (150°C)	Tysonite
$(\text{ZrF}_4)_{0.50}(\text{BaF}_2)_{0.35}(\text{CsF})_{0.15}$	3×10^{-6} (150°C)	Glass
$(\text{InF}_3)_{0.35}(\text{SnF}_2)_{0.30}(\text{PbF}_2)_{0.35}$	8×10^{-4} (150°C)	

Table 9 Classification of oxide-ion conductors

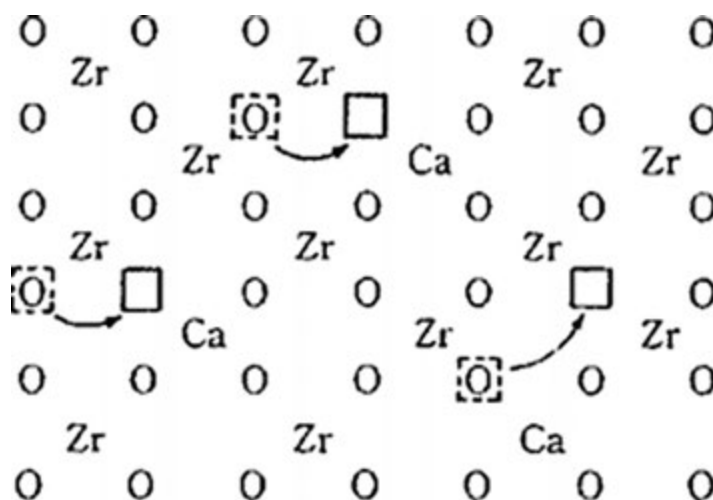
Crystal type	Host oxide	Example
<i>Fluoride-type</i>		
MO_2 -based	ZrO_2	$(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$
	CeO_2	$(\text{ZrO}_2)_{0.8}(\text{Sm}_2\text{O}_3)_{0.2}$
	ThO_2	$(\text{ThO})_{0.9}(\text{CaO})_{0.1}$
$\text{MO}_{1.5}$ -based	Bi_2O_3	$(\text{Bi}_2\text{O}_3)_{0.85}(\text{Nb}_2\text{O}_5)_{0.15}$
<i>Perovskite-type</i>		
Single perovskite	CaTiO_3	$\text{CaTi}_{0.7}\text{Al}_{0.3}\text{O}_{3-x}$
	LaGaO_3	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-x}$
Perovskite-related	$\text{Ba}_2\text{In}_2\text{O}_5$	$\text{Ba}_2\text{In}_{1.75}\text{Ce}_{0.25}\text{O}_{5.125}$
<i>Scheelite-type</i>	PbWO_4	$\text{Pb}_{0.8}\text{La}_{0.2}\text{WO}_{4.1}$

conductors. Another interesting example is $\beta\text{-Mg}_3\text{Bi}_2$, which has large diffusivity of Mg since the sublattice of small Mg is melting among the fixed Bi sublattice like $\alpha\text{-AgI}$ (Barnes *et al.*, 1994). H_xWO_3 which is used for electrochromic devices has large hydrogen mobility as well as high electronic conductivity.

Most important application of the ion-electron mixed conductors is the Solid Oxide Fuel Cells (SOFC) shown in Section Solid oxide fuel cell (SOFC), which works in very high temperature up to 800 to 1000°C where no metallic electrode is stable. Thus, the

Table 10 Classification of oxide-ion conductors

Crystal type	Host oxide	Example
Fluorite	ZrO ₂	(ZrO ₂) _{0.92} (Y ₂ O ₃) _{0.08}
	CeO ₂	(ZrO ₂) _{0.8} (Sm ₂ O ₃) _{0.2}
	ThO ₂	(ThO) _{0.9} (CaO) _{0.1}
	Bi ₂ O ₃	(Bi ₂ O ₃) _{0.85} (Nb ₂ O ₅) _{0.15}
Single perovskite	CaTiO ₃	CaTi _{0.7} Al _{0.3} O _{3-α}
	LaGaO ₃	La _{0.8} Sr _{0.2} Ga _{0.8} Mg _{0.2} O _{3-α}
	BaTiO ₃	Na _{0.5} Bi _{0.5} TiO ₃
Perovskite-related	Ba ₂ In ₂ O ₅	Ba ₂ In _{1.75} Ce _{0.25} O _{5.125}
Scheelite-type	PbWO ₄	Pb _{0.8} La _{0.2} WO _{4.1}

**Fig. 11** Mechanism of oxide ion conduction in stabilized zirconia.

electronic conduction of oxide ceramics are used for the electrode materials, which have also the conductivity of oxide ions (Fig. 12). As was shown in Section Oxide Ion Conductors, some oxide ion conductors have electronic (hole) conductivity under reduced or oxidative atmosphere, which is a drawback for the electrolyte but is useful for the electrodes.

Ceria-based oxide ion conductors as (CeO₂)_{0.8}(Sm₂O₃)_{0.2} and (CeO₂)_{0.8}(Gd₂O₃)_{0.2} become partially electronic conductors under a reducing atmosphere at high temperatures, where the ceria electrolytes are partially reduced and nonstoichiometric oxygen defects are formed with excess electrons which contribute to the electronic conduction. In general, the electronic conductivity of an oxide electrolyte at elevated temperatures is influenced by partial oxygen pressure (pO₂) surrounding them. The n type electronic conductivity σ_n increases with decreasing pO₂, whereas p type electronic conductivity σ_p increases with increase in pO₂. It is known that the relations between σ_n or σ_p and pO₂ are given by

$$\sigma_n = \sigma_n^0 \exp pO_2^{-1/n} \quad (9)$$

and

$$\sigma_p = \sigma_p^0 \exp pO_2^{1/n} \quad (10)$$

where n is a natural number, and σ_n^0 and σ_p^0 are constants which are independent of the partial pressure of oxygen. It is accepted that the ionic conductivity σ_i itself is rarely dependent on pO₂ for many oxide electrolytes. Accordingly, the total conductivity σ is expressed as,

$$\sigma = \sigma_i + \sigma_n^0 \exp pO_2^{-1/n} + \sigma_p^0 \exp pO_2^{1/n} \quad (11)$$

The relation between the logarithm of conductivity and logarithm of pO₂ is illustrated in Fig. 13. The hatched regions indicate the mixed conduction domains, and between them there exists an ionic conduction domain where the electronic conductivity is negligibly small. The outer sides of the mixed conduction domains are electronic conduction regions.

Some perovskite-type oxides containing transition elements exhibit mixed conduction at elevated temperatures. Doped-lanthanum cobaltites are mixed conductors in which oxide ions and holes are the charge carriers. The electronic conductivity is a few orders of magnitudes higher than that of the oxide ionic, although the ionic conductivity itself is sufficiently high ($> 1 \times 10^{-1} \text{ S cm}^{-1}$). High

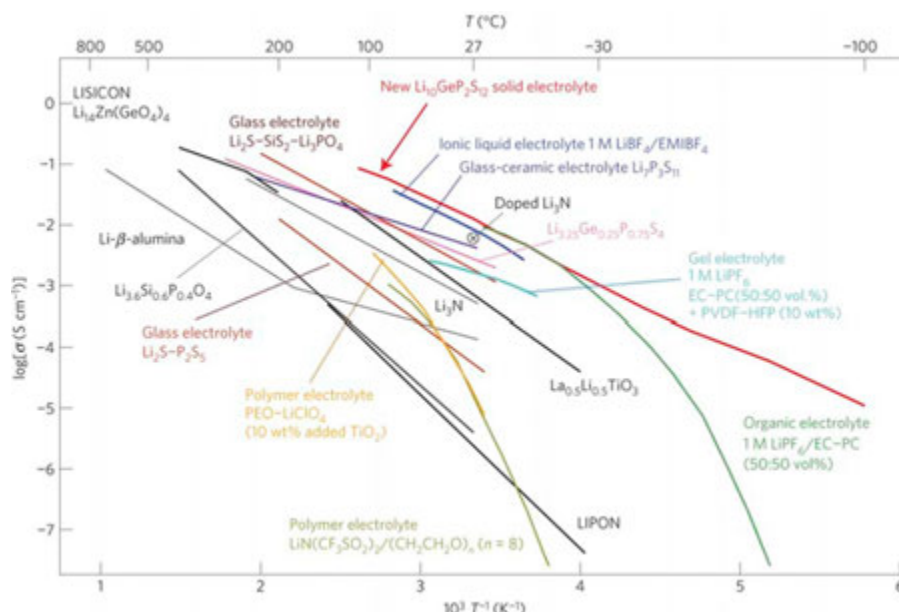


Fig. 12 Temperature dependence of conductivity of lithium ion (Kamaya *et al.*, 2011).

temperature-type protonic conductors based on, for example, SrCeO_3 and BaCeO_3 are a kind of mixed conductor under humidified air at high temperature. In this case, the charge carriers are both protons and electron holes.

Applications of Ion Conducting Solids

Benefits of Ion Conducting Solids for Applications

Ion conducting solids, ie, solid-state ionics materials are classified as solid electrolytes and mixed conductors, both of which have peculiar functions applicable in the field of advanced technologies. A solid electrolyte is a functional material in which mobile ions play an important role. In general, solid electrolytes have the following benefits:

- (i) They have both an electrical and a chemical function.
- (ii) They can serve both as ionic and structural materials.

With regards to point (ii) a solid electrolyte has a dual function, ie, it acts both as a structural material and as an ion conductor. In this sense, solid electrolytes are convenient compared to ion conducting liquids which need a container. With regard to (i) these materials conduct electricity while they simultaneously give rise to some chemical reactions at the surface of the electrolyte. Inversely, when different chemical reactions take place at both sides of the solid electrolyte surfaces, an electromotive force (EMF) is generated across the electrolyte.

Three Fundamental Functions Applicable to Devices

Ion conducting solid has the following three essential functions applicable to many electrochemical devices, ie, appearance of electromotive force, preferential permeation of a specific ion, and formation of large space charge.

An EMF is caused when a difference in concentration (or activity) of a specified chemical component is generated between the two sides of an ion conducting solid diaphragm. **Fig. 14** illustrates this phenomenon for the case of an oxide ion conductor. In this oxygen concentration cell the EMF, E , is given by

$$E = \frac{RT}{4F} \ln \frac{p_{\text{O}_2}(1)}{p_{\text{O}_2}(2)} \quad (12)$$

where $p_{\text{O}_2}(1)$ and $p_{\text{O}_2}(2)$ are the oxygen partial pressures in electrode compartment (1) and (2), respectively. This EMF phenomenon can be applied to chemical sensors and power cells (**Fig. 15**).

Fig. 16 shows a schematic illustration of the preferential permeation of oxygen in the case of an oxide ion conductor as an example. This function is based on a property that only one kind of ion can move in a solid electrolyte. Using this function, one can extract a specified element from a mixture or a molecule. This can be applied to the electrolysis of molecules and separation of specified gas from gas mixture. Formation of large space charge is caused by uneven distribution of mobile ions after an electric field was applied.

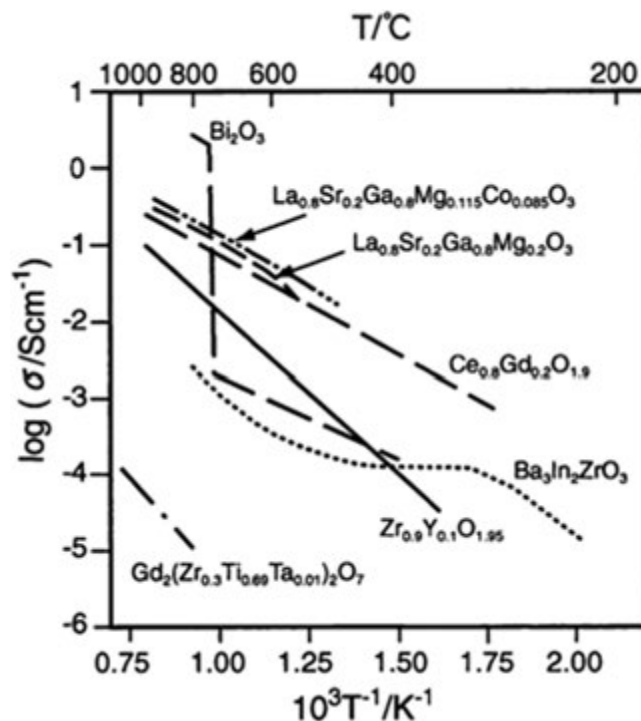


Fig. 13 Conductivity of typical oxide ion conductors (Sasaki, 2013).

Application Examples

There are many possible applications of ion conducting solids. First group is chemical sensors; for example, oxygen gas sensors for automobile engine control or steel making, NO_x sensors and cleaner for exorst gas controle, CO_2 sensors. Second group is electrochemical energy sorces such as lithium ion battery, NaS battery and various fuel cells. Third kind is for ion transfer membrane for gas purification, electrochemical reactors. Fourth kind is for electronic devices as electrochromic display, or atom-switch etc. Some of them are depicted below.

(a) Sensors

The appearance of an EMF across a solid electrolyte is based on the principle of an electrochemical cell or battery. The batteries for practical use are classified into "signal" cell and "power" cell. The signal cell is used as a sensor for measuring the concentration of a specified material. For example, with regards to oxygen, if $p\text{O}_2$ (1) in Eq. (12) is known and is constant, the partial pressure of oxygen in compartment (2) can be determined from the EMF of the cell and this functions as an oxygen sensor. Oxygen sensors using stabilized zirconia as an oxide ion conductor are now widely used for the analysis of exhaust gases from engines, industrial furnaces, respiration, etc. This sensor works at temperatures higher than 400°C . At lower temperatures the electrode polarization and ohmic resistance are too large to give an exact EMF of the cell. They are also used to probe the oxygen activity in molten iron in the steel making process. Besides the oxygen sensors, a fluoride ion sensor using fluoride ion-conducting solid LaF_3 and a sodium sensor using Na β -alumina are in practical use. A hydrogen sensor for molten aluminum in industrial casting processes has been developed using the proton conducting ceramic of $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-x}$. SO_x and NO_x sensors using sodium ion conductor or oxide ion conductors with sulfates or nitrates as auxiliary materials are developed.

(b) Lithium ion batteries

After the invention of rechargeable Lithium Ion Batteries (LIB) in 1980, they have been used in mobile phone, PC, tablet, etc., for IT devices and now for plug-in-hybrid (PHV) and electric vehicles (EV). For this purpose, the lithium ion transport in solids, liquid, polymer and gels has been widely investigated. A conventional lithium ion battery consists of lithium transition metal oxide (eg. LiCoO_2 , LiMn_2O_4 , LiFePO_4 , etc.) for cathode, lithium carbon (Li_xC) or lithium alloys (Li_xSn , Li_xSi , etc.) for anode, and organic liquid electrolyte (EC + DMC + LiPF_6 , etc.). Those cathode and anode materials are considered as ion-electron mixed conductors as shown in Section Mixed Ionic-Electronic Conductors, although whose ionic conductivity is much smaller than the electronic one.

If the liquid electrolyte of the LIB is replaced by a solid electrolyte, an all-solid state lithium battery can be constructed, which has a big merit on safety and long life stability. For this purpose, sulfide based solid electrolytes such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and similar glasses are developed as the first candidate since its conductivity is as high as conventional liquid electrolytes. However, it is rather unstable against the contact to lithium metal and water. Oxide based solid electrolytes such as LIPON, LLZ etc., are the other

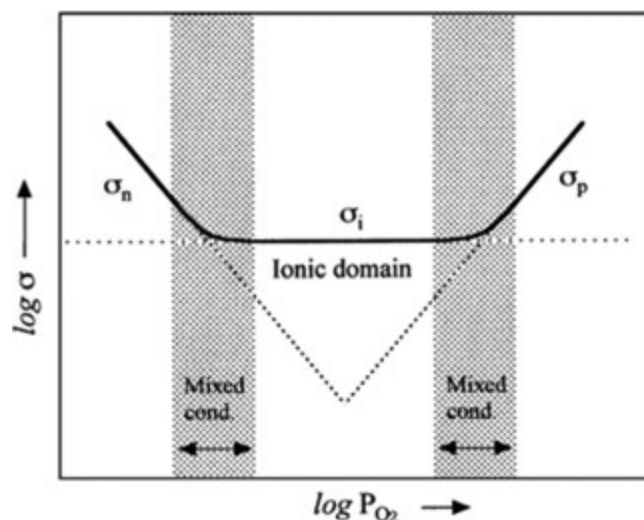


Fig. 14 Dependence of conductivity on oxygen partial pressure in the case of mixed conducting oxides.

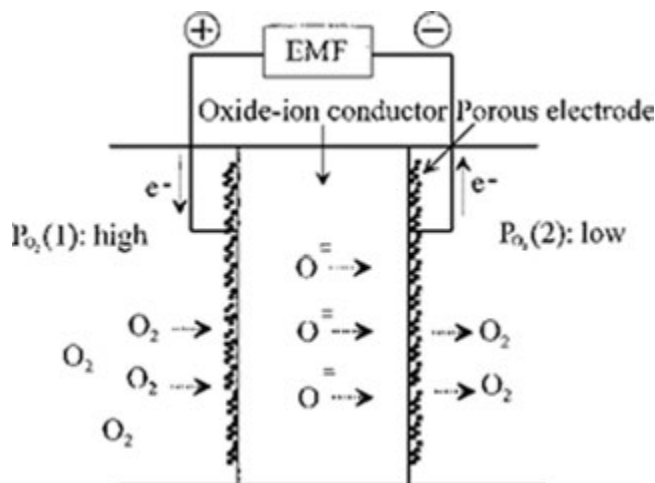


Fig. 15 EMF of oxygen concentration cell.

candidates, which are stable to lithium metal although the conductivity is lower than the sulfides. In order to reduce the resistance of the solid electrolyte, thin film technology is developed to construct all-solid-state thin-film batteries (TFB), in which the electrolyte thickness is 1 μm or less and the total thickness is less than 100 μm (see Fig. 17). In spite of the small capacity of the TFB it is now recognized very suitable for micro wearable or implant devices as well as energy harvesting applications.

(c) NaS battery

Because of the larger natural abundance of sodium than lithium, many studies are under going to construct large scale sodium batteries for mega watt (MW) class. The principle of the sodium battery is similar to that of lithium, however the higher reactivity of sodium hampered the development. Only so called NaS battery is commercially available at present. The working principle of a NaS battery is shown in Fig. 18. A single cell is made of a Na β'' -alumina ceramic tube containing liquid sodium metal and surrounded by molten sulfur. The cell is sealed in a stainless steel tube working as a current collector. The cell is working above 300°C to keep the sodium and sulfur in molten state. Single cell voltage is 1.8 V and the capacity of 1220 Wh, which is assembled to 384 cells of 400 kWh. Farther assembling them to construct large scale energy storage system up to 50 MW is developed by NGK Insulators, LTD, Japan, which is now widely used for back-up system and load leveling of wind and solar energies.

(d) Solid oxide fuel cell (SOFC)

The principle of the SOFC is shown in Fig. 19, where the hydrogen gas reacts with oxide ions in solid electrolyte (eg, YSZ) to produce water and electricity. This type of power generator is, in principle, very high in efficiency, clean in exhaust gas, and silent to run. Siemens-Westinghouse Co. have developed 100 kW-scale SOFC. JX and Tokyo Gas have sold s SOFC of max. 700 W for home

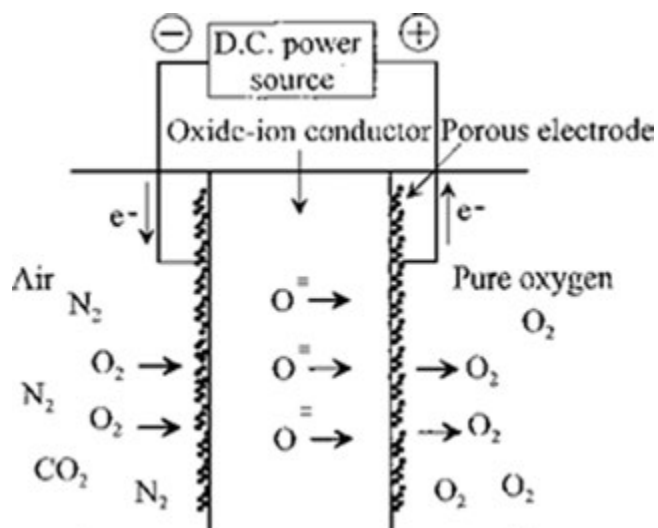


Fig. 16 Oxygen purification by oxide ion conductor.

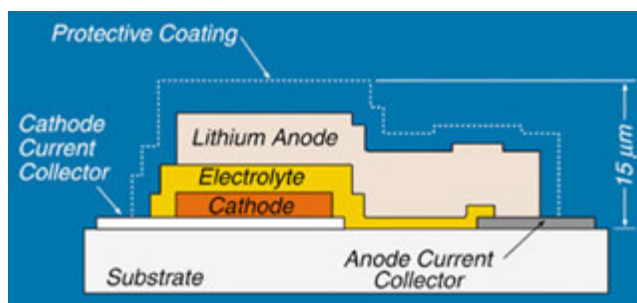


Fig. 17 Concept of all-solid-state thin-film lithium battery (Bates *et al.*, 2000).

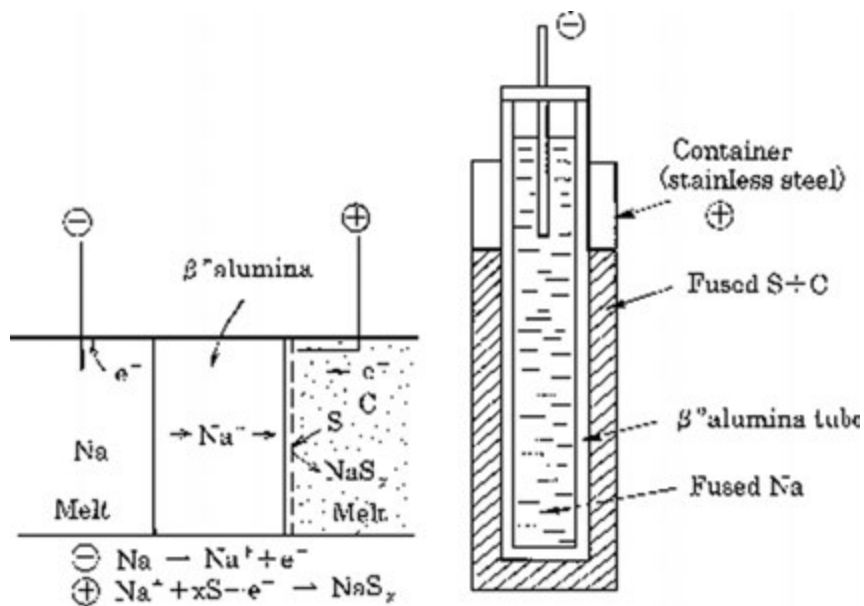


Fig. 18 Concept and structure of NaS battery.

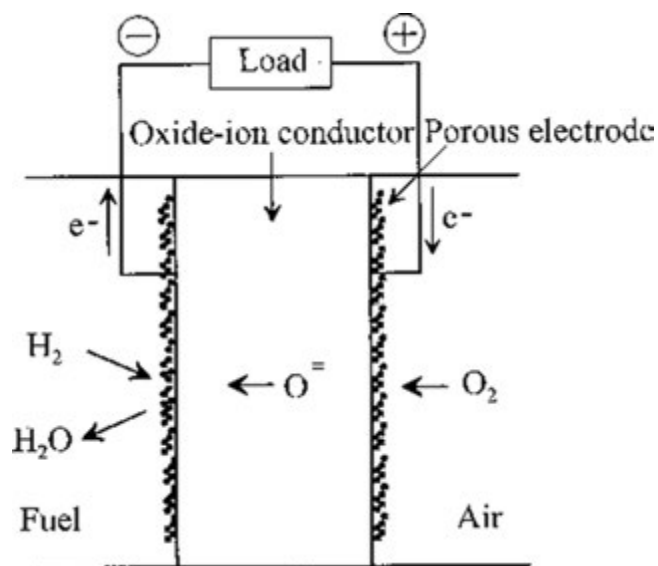


Fig. 19 Concept of solid oxide fuel cell (SOFC).

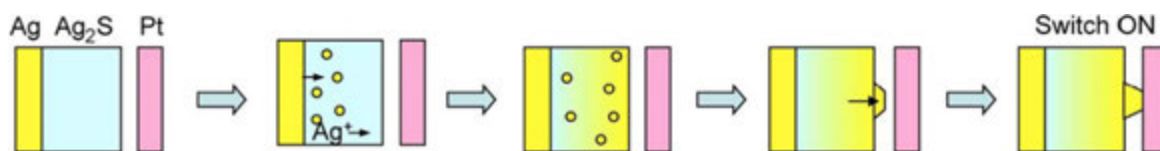


Fig. 20 Principle of atomic switch (Aono and Hasegawa, 2010).

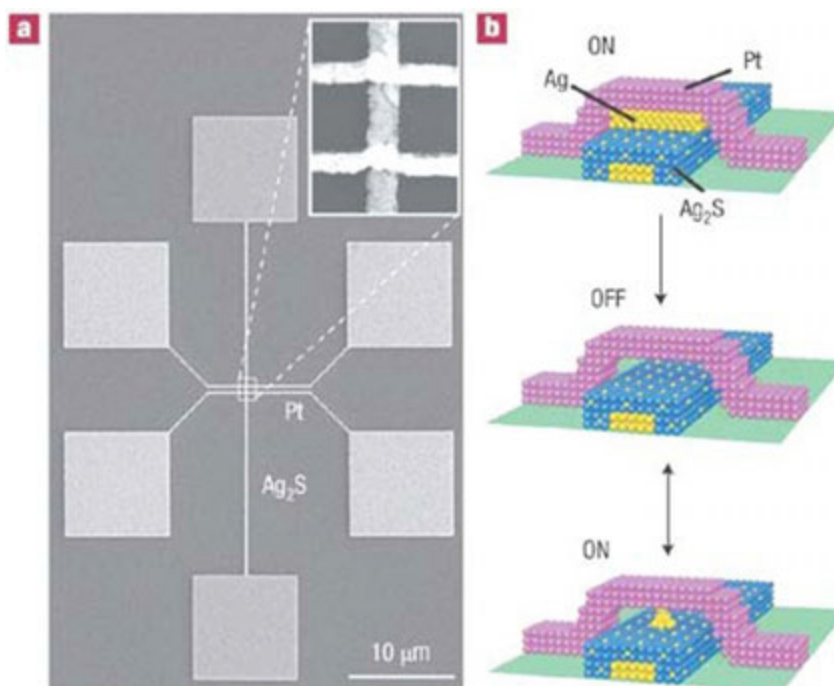


Fig. 21 An example of nano-ionics switch architecture (Wase and Aono, 2007).

stationary use, which is equipped with reforming system of natural gas to hydrogen and cogeneration system to use the exhaust heat for hot water supply.

(e) Electrolysis of gaseous molecules

If a fuel cell is operated inversely, hydrogen is obtained from steam; for example, polymer electrolyte type PEM electrolyzer and solid oxide electrolyzer cell (SOEC) are known. This method is a promising way to produce hydrogen effectively in large scale, and will be a powerful tool for the future age of hydrogen economy, however the efficiency and cost are still the neck for practical use. Steam electrolysis is also possible using proton conducting ceramics. In this case pure hydrogen free from water vapor is obtained.

(f) Gas separation

By using oxide ion conductors or proton conductors, pure oxygen or hydrogen gas can be obtained in a one-step operation as shown in Fig. 16. Electrochemical oxygen pumps made of stabilized zirconia are on the market. This device can pump up or add oxygen gas preferentially from or to a gas mixture and is utilized in many laboratories. A hydrogen pump which uses proton-conducting ceramics is in development.

(g) Atomic switch or nano-ionics circuits

Electrochemical deposition of metals from solid electrolyte is common phenomena in solid state ionics, however whose nano-scale control is now open the door to new electric circuit technology called "Atomic Switch" (Aono and Hasegawa, 2010), "Nanoionics switch" (Wase and Aono, 2007). The principle is shown in Fig. 20, where Ag metal wire works as a source of silver ions and Pt metal is the collector of deposited silver metal filament. Ag₂S is an ionic-electronic mixed conductor which works as a transfer channel of silver ions and also electronic current conductor when the switch is on. When the top Ag electrode is positively biased and Pt is negative, a potential difference appears on the gap between the Pt and Ag₂S, which generates the accumulation of silver ions in the Ag₂S and finally the oversaturated silver metals start to form a small needle at the bottom of the Ag₂S. The needle finally contacts to the Pt electrode and the both electrodes are short circuited. When the potential bias is reversed, the precipitated silver needle between the Ag₂S and Pt is absorbed into the Ag₂S and the circuit is now open. Starting from this principle, many circuit designs are now proposed. A prototype device design is shown in Fig. 21. These phenomena are reversible in nano-scale and is used for a memory device, switching device, synaptic switch etc. For this purpose, not only the Ag₂S but many ionic conductors and mixed conductors have been tested now.

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Possibility of Using Carbon Nanotubes in Water and Wastewater Treatment

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Glossary

CCVD Catalytic chemical vapor deposition.

CNTs Carbon nanotubes.

CVD Chemical vapor deposition.

DWCNTs Double walled carbon nanotubes.

HA-CNTs Horizontally aligned carbon nanotube tubes.

MWCNTs Multi walled carbon nanotubes.

NOM Natural organic matter.

SWCNTs Single walled carbon nanotubes.

VA-CNTs Vertically aligned carbon nanotube tubes.

WHO World Health Organization.

Introduction

The number of inhabitants on our planet is increasing rapidly, and the need for food and water is increasing even faster. Given that the amount of fresh water in the world is decreasing, and that fresh water used in drinking is getting more and more polluted, it is necessary to find new sources from which fresh water can be obtained (Roy and Bhattacharya, 2015).

Water is one of the most important basic substances in nature and it is necessary for the maintenance of plants, animals and human lives. Technological progress of the 21st century has caused the exhaustion of natural resources, pollution of the atmosphere, water and environment, destruction of vegetation, etc., which has a negative impact on human health (Ahmad *et al.*, 2016).

Quantity and nature of wastewater directly affect the recipient in terms of disturbance of the natural balance of aquatic ecosystems and direct threats to the environment. Wastewater is usually a complex mixture of organic and inorganic components, as well as different hazardous substances (Sharma and Bhattacharya, 2017). It is one of the main polluters of surface and groundwater, which are the natural sources of drinking water. This applies particularly to industrial wastewater and other establishments (Šušteršič, 2014; Roy and Bhattacharya, 2015).

Treatment of drinking water involves the use of various processes and operations, which eliminate some deficiencies of raw water, sometimes the whole complex of defects. Sometimes it artificially improves the specific characteristics required by consumers, that is, the standards that set the quality criteria for drinking water (Gehrke *et al.*, 2015). Methods for drinking water treatment include a number of main and supplementary processes and operations that are combined in the technological process, often with special treatment, whose conditioning scheme can be very simple (for example, only water disinfection), but also extremely complex. Conventional technologies are primary (screening, filtration, centrifugation, separation, sedimentation, coagulation and flocculation); secondary (aerobic and anaerobic treatments); and tertiary (distillation, crystallization, evaporation, solvent extraction, oxidation, precipitation, ion exchange, reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), adsorption, electrolysis and electro dialysis level water treatment technologies) (Amin *et al.*, 2014; Šušteršič, 2014; Das *et al.*, 2014b; Upadhyayula *et al.*, 2009).

Adsorption is one of the most widely used methods for water and wastewater treatment to remove various pollutants. However, the low capacity and short cycle of sorption, short lifespan and limited surface, present some of the problems in the use of water treatment (Werkneh and Rene, 2019). Today, a large number of researches are focused on finding new materials that can be used as adsorbents. Carbon materials are classified as some of the most important and widely used adsorbents (Li *et al.*, 2007; Amin *et al.*, 2014). Unlike conventional adsorbents, they have a large specific surface, outturn fast kinetics, have a specific affinity towards different pollutants and possess high reactivity (Gehrke *et al.*, 2015; Werkneh and Rene, 2019).

Membrane processes, ultrafiltration and reverse osmosis (Giwa *et al.*, 2016) are being used more and more for the separation and fractionation of organic and inorganic substances from aqueous solutions. This field of application was mainly in the desalination of seawater for the needs of settlements and cities (Corry, 2008), but it is increasingly expanding on the field of water treatment for medical and pharmaceutical purposes. The quality of the membrane and the operating pressure of the plant depends on the degree of water purification, capacity, economy and purpose of the plant (Raffi *et al.*, 2012).

Membrane Filtration

Membrane filtration is used for removal of colloidal and particulate matters from drinking water and wastewater. Membrane filters are designed and manufactured using various materials (Le and Nunes, 2016). In general, the material is selected based on two key factors: the size of the pores and durability. The smaller the pore size, then the smaller particle will be blocked to pass through the membrane filter. Durability refers to the ability of the membrane to function and maintain the conditions to which it is exposed (El Saliby *et al.*, 2011). The usual filtration processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). In Table 1 characteristics for different membrane processes are shown.

Table 1 Characteristics of different membrane processes

Membrane process	Pore size (nm)	Pressure (MPa)	Membrane materials	Removed material	Water permeability ($L m^{-2} h^{-1} bar^{-1}$)	Footnote citations
Microfiltration (MF)	50–500	0.05–0.2	cellulose acetate, polyvinylidene fluoride, polyacrylonitrile, polypropylene, polysulfone, polyethersulfone, or other polymers	sand, silt, clays, oil emulsion, algae and some bacterial species	>50	^A
Ultrafiltration (UF)	2–50	0.1–1	The same as MF	all microbiological species removed by MF, proteins, some viruses and humic materials	10–50	^B
Nanofiltration (NF)	≤2	1–4	cellulose acetate, polyamide materials	all cysts, bacteria, viruses, and humic materials	1.4–12	^C
Reverse Osmosis (RO)	0.3–0.6	3–7	cellulose acetate, polysulfone, polyvinylidene fluoride or other polymers, polyamide materials	almost all inorganic contaminants from water, radium, natural organic substances, pesticides, cysts, bacteria and viruses, heavy metal, natural organic substances, bacteria and viruses	0.05–1.4	^D
Carbon nano-tubes membranes	0.1–2	negligible	CNTs and polymers in VA and MWCNT		SWCNT- 13.2, MWCNT – (0.6–0.84)	^E

^{A, B, C, D}Ali *et al.* (2019a); Giwa *et al.* (2016); Le and Nunes (2016); Pendergast and Hoek (2011); Scott (1995); Budimirović *et al.* (2017).

^ELee *et al.* (2015); Das *et al.* (2014a,b); Khan *et al.* (2016).

In the last few decades, the development of membrane separation processes has been noticeable, which is replacing more and more conventional plants in various industrial processes (Giwa *et al.*, 2016). Compared to conventional separation processes, membrane processes allow for greater separation efficiency of desired components and uniform distribution of fluid flow at the inlet and device without additional elements. Effective application of membrane processes is well known in the field of environmental protection, desalination, removal of harmful gases and separation of components that can hardly be separated by conventional separation processes, in the water treatment for food and pharmaceutical industry and for other needs (Le and Nunes, 2016).

Microfiltration is a low-pressure process and is used to separate large colloidal particles from aqueous solutions by means of semi-permeable membranes. The application of microfiltration also includes wastewater treatment (Roy and Bhattacharya, 2015), where in addition to the separation of solids, it can be also used to remove finely dispersed oils in wastewater (Aleksić *et al.*, 2016). Microfiltration can be used as a replacement for coagulation, flocculation, sedimentation (Chae *et al.*, 2008), and filtration which are pre-treatment processes in the conventional water treatment in the food and paint industries. In addition, microfiltration is often used as a pre-treatment of raw water in NF and RO membrane systems (Valavala *et al.*, 2011).

Similarly to the microfiltration, ultrafiltration is a low-pressure process which can be used to separate large particles from aqueous solutions. Some oil emulsions, soot particles, sugar particles, endotoxins, viruses, colloids, some enzymes and proteins, as well as some soluble salts are retained.

Nanofiltration is a process that takes place under low to moderately high pressures, with monovalent ions passing freely through the membrane, while the membrane significantly repels multivalent salts and low molecular weight molecules (Shon *et al.*, 2013). Typical application of nanofiltration is in water supply, desalination, wastewater treatment, in water softening processes, as well as in the removal and processing of acidic solutions. Pendergast and Hoek (2011), grouped all types of membranes which are used in nanofiltration into three categories:

- (1) nanostructured ceramic membranes,
- (2) organic/inorganic membranes,
- (3) biologically inspired membranes.

Nanostructured ceramic membranes can be synthesized from ceramic materials such as zeolites, carbon nanotubes and graphene (Humpalik *et al.*, 2011). Ceramic membranes have good mechanical, chemical and temperature resistance, but their price is high (Amin *et al.*, 2012).

Organic membranes are polymeric membranes and are made of polysulfone, polyethersulfone, cellulose acetate, polymethylpentene, polyimide, polyetherimide, etc. while inorganic membranes can be ceramic, metallic, zeolite or carbon membranes. Today, organic membranes are mostly widespread on the market, because they have low prices, but also have low mechanical stability and fouling problems. Inorganic membranes are made from row inorganic materials such as a metal oxide mixtures (Al_2O_3 , ZrO_2 , TiO_2 , and SiO_2) and these membranes are most widely used for applications in purification, wastewater treatment and desalination. They have a good chemical and mechanical stability, thermal resistance, long lifetime and also reusability (Chen *et al.*, 2017).

Biologically inspired membranes are made up of a set of smaller molecules and can be hybrid protein-polymer biomimetic membranes, aligned nanotube membranes and iso-porous block copolymer membranes (Pendergast and Hoek, 2011). They are not yet commercially available, but they do offer significant performance improvements.

Desalination

Desalination is the process where the result is the fresh water produced from brackish or seawater. Desalination technologies can be used for a number of applications, but the main purpose is to produce potable water from saline water for domestic or municipal purposes. Conventional methods to remove salt from the water are precipitation, oxidation, reduction, ion exchange, membrane filtration and adsorption, but these techniques are not very effective in removing salt from the water. Therefore, today, the possibility of using nanomaterials in this area is being investigated because it requires less pressure, lower energy consumption and high salt dissolution (Cotruvo, 2004).

The most common desalination method is "reverse osmosis". Reverse osmosis process (RO) is relatively more effective than NF, however, it needs more energy than NF for its functioning, and for that reason it is less attractive (Amin *et al.*, 2014). In the reverse osmosis process, semipermeable membranes are used to filter dissolved salts and fine solids at high pressure, using a large amount of energy (Corry, 2008). Today, RO plants represent the global desalting capacity and are the fastest growing desalination method, with high productivity, high salt rejection and relatively low membrane cost. From 1999–2018, the total number of globally installed desalination plant increased from 11,000 with capacity of 20 million $\text{m}^3 \text{ day}^{-1}$ to 20,000 plants and capacity over 100 million $\text{m}^3 \text{ day}^{-1}$ in 150 countries (see Relevant Websites section; Cotruvo, 2004). Also, membranes are prevailing on the market with over 90% (see Relevant Websites section). Usually, for RO membrane materials are used polyamides, polysulfones, polymeric materials like cellulose triacetate (Cotruvo, 2004; Mohamed, 2011), and new materials are graphene oxide (Kim *et al.*, 2018), carbon nanotubes (Ali *et al.*, 2019a; Ma *et al.*, 2017), nanoporous graphene (Cohen-Tanugi and Grossman, 2015) and aquaporin (Tang *et al.*, 2013).

Nanotechnology for Water and Wastewater Treatment

Many developing countries are using unconventional water sources for drinking water, and also many countries are using centralized water treatment system with conventional techniques which are not efficient in removing many pollutants (Machado *et al.*, 2019).

Today nanotechnology has become one of the world's best technologies. The term nanotechnology describes the whole range of technologies that are now applied in different industries (Kanchi, 2014). This technology uses nanoparticles (ISO/TS 80004-2:2015), which are generally defined as those particles with at least one dimension in the nanoscale size range, which is from 1 to 100 nanometers (nm) (ISO/TS 27687:2008). Every year, an increasing number of researchers are dealing with nanotechnology, nanomaterials, their applications and problems that may arise from their use.

The nanomaterials for the water treatment can be divided into three main groups: nano-adsorbents, nanocatalysts and nano-membranes (Gehrke *et al.*, 2015; Machado *et al.*, 2019). All types of nanomaterials can be used for removal of organic and inorganic pollutants from drinking water, heavy metal ions and dye from wastewater and for desalination (Ali *et al.*, 2019a; Das *et al.*, 2014b; Lu and Chui, 2006; Fard *et al.*, 2018 etc).

Carbon Nanotubes

Almost thirty years have passed since the discovery of carbon nanotubes (CNTs) (Iijima, 1991). Although for today's science is not a short period, carbon nanotubes, thanks to their exceptional properties continue to represent great potential for research. Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure with open or closed ends (Samal and Bal, 2008). CNTs membranes can be used as high quality adsorbents for removal of biological, as well as heavy metal contaminants commonly found in water treatment plants (ions arsenic, lead and cadmium) (Ali *et al.*, 2019a; Amin *et al.*, 2014). Nanomaterials have a number of specific properties compared to conventional materials. A large specific surface is the key feature for their application in the treatment of wastewater and the preparation of drinking water (Das *et al.*, 2018). Due to the large specific surface area, nanomaterials have a higher number of active sites for interaction with different chemical species, which makes them one of the most efficient adsorbents (Sadehgh *et al.*, 2017).

Carbon nanotubes (CNT) are macromolecules of cylindrical shape with a radius of only a few nanometers and a length of up to 20 cm (Das, 2013). One of their most promising application is certainly in the treatment of water as adsorption material due to the large specific surface and porous structure of the full cavity. The adsorption capacity of CNTs depends on the experimental conditions, nature and type of adsorbent (Sadehgh *et al.*, 2017). Despite this, the pristine CNTs have very low adsorption capacity for metal ion because of their hydrophobic character.

Structure, Properties and Synthesis of CNTs

Carbon nanotubes can be constructed in two basic forms, single-walled and multi-walled carbon nanotubes (Prasek *et al.*, 2011; Karthik *et al.*, 2014).

Single-walled carbon nanotubes (SWCNT) are essentially a wrapped sheet of graphene in a cylinder of 1–2 nm in diameter and a length of even a few micrometers (De Volder *et al.*, 2013). Because of the large ratio of length and diameter, the SWCNTs act practically as one-dimensional ones. Special type of nanotube with only two rolled up graphene layers are double-walled carbon nanotubes (DWCNTs) and are approximately same as those of SWCNTs, but their resistance to chemicals is much better (Karthik *et al.*, 2014). Depending on wrapping, SWCNTs can have armchair, chiral, and zigzag form (Eatemadi *et al.*, 2014) and the wrapping method determines almost all the properties, so, depending on this, they may act as conductors or semiconductors.

Multi-walled carbon nanotubes (MWCNT) consist of several twisted layers of graphite around the same axis with diameter of 5–20 nm (De Volder *et al.*, 2013). The inter-layers distance in the MWCNTs is 0.34 nm, which is also the distance between the two parallel graphene layers in the graphite (Peigney *et al.*, 2000; Nessim, 2010). With MWCNT, the ratio of length and width is usually about 100:1 and the diameter is a few dozen nanometers. The structure of MWNT is not so well understood due to its complexity and it is also the main reason why it is not produced in significant quantities, although its production is simpler and it is cheaper than the SWCNT. In their structure, imperfections can be found (defective sites), which leads to degradation of material properties, such as strength and electronic properties (Table 2).

The main advantageous characteristics of CNTs are good structural, optical, thermal and mechanical features. These properties include good electrical and thermal conductivity, density, lattice structure and depend on diameters, number of walls, chiralities, and defect densities, etc. (Zhang *et al.*, 2017).

The applications of CNTs are of very wide range: from biomedical devices, drugs delivery and therapies, cosmetics (Eatemadi *et al.*, 2014; Madani *et al.*, 2013), automotive industry (De Volder *et al.*, 2013), electronics (Khan *et al.*, 2016), desalination (Ali *et al.*, 2019a; Corry, 2008) and water and wastewater treatment (Ahmad *et al.*, 2016; Ma *et al.*, 2017; Roy and Bhattacharya, 2015).

In order to prepare SWCNTs and MWCNTs, usually three synthesis methods are used: arc discharge, laser ablation (Prasek *et al.*, 2011) and chemical vapor deposition (CVD) (Rafique and Iqbal, 2011; Ma *et al.*, 2017; Nessim, 2010). However, researchers are also analyzing others methods such as a catalytic chemical vapor deposition (CCVD) (Magrez *et al.*, 2010), high pressure growth

Table 2 Types and characteristics of CNTs

<i>Types of CNTs</i>	<i>Positive characteristics</i>	<i>Negative characteristics</i>	<i>Footnote, citations</i>
Single-walled carbon nanotubes – SWCNTs	– High strength, – Large active specific surface area, – Strong antimicrobial activity, – Good electrical properties (high conductivity), – Good corrosion stability, – They are effective as thermal insulators, – Mechanical properties: 640–1054 GPa for Young's modulus and 150–180 GPa for tensile strength.	– Complicated fabrication (depends on the synthesizing method), – Purity is poor, – A chance of defect is bigger during functionalization, – Possible health risks, – Possible environmental risks.	A
Multi-walled carbon nanotubes – MWCNTs	– Higher tensile strength than SWCNT – Thermal and chemical stability – High purity – Less effective than SWCNT in cell inactivation, – Smaller antimicrobial activity.	– Cannot be easily twisted, – Very complex structure, – Possible health risks.	B
<i>CNTs membrane types</i>	<i>Positive characteristics</i>	<i>Negative characteristics</i>	<i>Footnote, citations</i>
Vertically aligned CNTs – VACNTs	– High energy absorption, – Compressive strength, – Recoverability, – Super-hydrophobicity with light weight, – Water flux rate is high.	– Complicated fabrication procedure: (It requires the use of low surface area flat catalyst supports during synthesis) Their ends must be opened, which also requires harsh conditions	C
Horizontally aligned CNTs – HACNTs	– Highly porous structure, – Large specific surface area, – High adsorption of NOMs, – Strong antimicrobial activity.	– The same as VACNTs	D
Mixed CNTs	– High filtration capability, – Antifouling propensity, – Simple fabrication process.	– Selectivity does not improve, – Additional cost for filler materials	E

^{A, B}Das *et al.* (2014a); Eatemadi *et al.* (2014); Gehrke *et al.* (2015); Vuković *et al.* (2009); Zhu *et al.* (2019).

^CDas *et al.* (2014b); Roumeli *et al.* (2019); Chen *et al.* (2010); Rashid and Ralph (2017).

^{D, E}Ali *et al.* (2019a); Lee *et al.* (2015); Pendergast and Hoek (2011); Zhang *et al.* (2017).

carbon monoxide reaction (HiPCO) (Bronikowski *et al.*, 2001; Rashid and Ralph, 2017), pyrolysis method and plasma enhanced CVD (PECVD) (Chen *et al.*, 2010). The arc-discharge method synthesis of carbon nanotubes is through arc-induced vaporization of two graphite electrodes placed end to end, separated by approximately 1 mm, and usually filled with inert gas (argon or helium) at low pressure (Khan *et al.*, 2016). For the arc discharge and laser ablation methods high temperature ($>1700^{\circ}\text{C}$) is necessary to provide high quality production and finish perfect nanotube structures. However, the manufacturing costs are very high which limits its wider manufacturing (Jeon *et al.*, 2011). Chemical vapor deposition (CVD) (Zhang *et al.*, 2017) is widely used method of producing CNTs because it is a simple and economic technique for synthesizing CNTs. Its uses methane, carbon monoxide or acetylene as carbon source with a metal catalyst particle (usually, cobalt, nickel, iron, or a combination of these such as cobalt/iron or cobalt/molybdenum) at low temperatures ($<800^{\circ}\text{C}$) (Eatemadi *et al.*, 2014; Rashid and Ralph, 2017). Szabó *et al.* (2010) have provided a detailed overview of the various techniques for the synthesis of CNTs in their paper.

Thermal and plasma-enhanced chemical vapor deposition are most commonly used to grow aligned CNTs (Szabó *et al.*, 2010). There are two mechanisms of growth aligned CNTs depending on the fact if the catalytic particle is lifted with increasing nanotube: "type-growth" and "base-growth" or not (Prasek *et al.*, 2011). The tip-growth mode is better than the base-growth mode for the high-speed growth of defect-free ultralong CNTs, but base-growth is better to obtain horizontally aligned carbon nanotube tubes (HA-CNTs) arrays with high areal density (Zhang *et al.*, 2017; Chen *et al.*, 2010). HA-CNTs are CNTs that are grown on flat substrates and parallel with each other with large intertube distances and lengths, while vertically aligned carbon nanotube tubes (VA-CNTs) are positioned normally to a substrate surface. Also, numerous authors analyze the possibilities of growth, synthesis and application of HA-CNTs and VA-CNTs (Ali *et al.*, 2019; Chen *et al.*, 2010; Roumeli *et al.*, 2019). HA-CNTs find applications in building blocks for transparent displays, nano electronics, quantum lines, field emission transistors, aeronautics (Zhang *et al.*, 2017) and VA-CNTs find applications in biomedicine and engineering for nanostructured filters, water treatment, separators, micro-electronics, diagnostic or therapeutic function (Chen *et al.*, 2010).

Functionalization of CNTs

Based on different ways of synthesizing carbon nanotubes, purification of the obtained material is very important because CNTs contain some carbonaceous impurities and metal catalyst particles (Hou *et al.*, 2008). Different methods are used to evaluate the purity of CNTs such as a scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Raman spectroscopy and ultraviolet visible-near infrared (UV-vis-NIR) spectroscopy (Hou *et al.*, 2008).

Usually, the purification methods are chemical (different types of oxidation), physical (or mechanical- filtration, centrifugation, solubilization and other technique to remove metal particles) and combination of both types of purification (microfiltration in combination with oxidation, sonication in combination with oxidation and others) (Hou *et al.*, 2008; Zare *et al.*, 2015). The conditions, duration and temperatures at which the purification process is carried out must always be selected appropriately, depending on the type of material being used.

Chemical modification (or functionalization) (Das, 2013) of CNTs is performed in order to improve the efficiency of pollutant removal, to increase application of CNTs in water or wastewater treatment and to facilitate membrane fabrication (Das *et al.*, 2014a,b; He *et al.*, 2013; Li *et al.*, 2007). Khan *et al.* (2016) divide chemical functionalization into covalent functionalization, non-covalent functionalization and endohedral functionalization. Chemical functionalization of CNTs is based on the covalent bond of functional groups (Jeon *et al.*, 2011). It can be divided into direct lateral wall covalent functionalization and indirect covalent functionalization with carboxyl groups on the CNT surface (Upadhyayula *et al.*, 2009).

Direct covalent functionalization of CNTs is most commonly done by oxidation method. Oxidation methods are often used to purify nanotubes because of their practicality, relative simplicity, applicability to metal catalysts and amorphous carbon, as well as the ability to purify large amounts of nanotubes. Different oxidants were utilized to treat the CNTs with HNO_3 , KMnO_4 , H_2O_2 , NaOCl , H_2SO_4 , KOH , and NaOH (Ali *et al.*, 2019a; Li *et al.*, 2007) and during the process carboxylic groups on the surface and the open sides of CNTs are formed. Functionalization of CNTs generates mainly the functional groups ($-\text{OH}$, $-\text{COOH}$, $-\text{C}=\text{O}$, etc.) thus increasing the negative charge on the surface of CNTs. This, on the one hand increases their dispersion in water, and on the other hand increases their affinity for adsorption of heavy metals, due to the transfer of charge between functional groups and metal cations (Li *et al.*, 2007).

Non-covalent functionalization of CNTs is based on the formation of supramolecular complexes using different adsorption forces such as van der Waals forces and π - π interactions. Compared to chemical functionalization, non-covalent functionalization has the advantage that it can take place under mild reaction conditions and has no effect on the electronic structure of nanotubes, whose special electronic and optical properties thus remain preserved. Non-covalent CNTs interactions involve the formation of non-covalent aggregates with surfactants (surfactant molecules), nanotube wrapping with polymers, including DNA (Sánchez-Pomales *et al.*, 2010), non-covalent biomolecule interactions and nanotubes (Jeon *et al.*, 2011).

Endohedral functionalization involves the placement of atoms or small molecules in the inner cavity of the nanotubes.

However, aggressive chemical functionalization, such as the use of concentrated acids at high temperatures, causes damage of nanotubes, resulting in changes in the length to diameter ratio and changes their dispersible properties. This is why many purification processes are performed in two stages, and the combination of different techniques and treatments allows for a high degree of achieved purity of carbon nanotubes.

Application of Carbon Nanotube in Water and Wastewater Treatment

In the water and wastewater treatment and also desalination, CNTs could be used as adsorbents, catalyst, filters and membranes (Ahmad *et al.*, 2016; Das *et al.*, 2014b; Liu *et al.*, 2013). One of the limiting factor in the mass production of CNTs is the price, because they are still relatively expensive.

Removal Pollutants

The chemical composition of natural water on the Earth is not unique and is created as a result of the interaction of water with minerals, soil and atmosphere, where various processes such as dissolution, chemical and biochemical reactions, as well as colloidal-chemical interactions are performed. In addition to natural factors, the chemical composition of water has an increasing impact on people through various anthropogenic activities, the most frequent being the discharge of insufficiently treated municipal and industrial wastewater into surface watercourses, as well as agricultural activities that have a major impact on groundwater. In the last few decades, the presence of heavy metals in ground and surface water has attracted the attention of researchers due to the exceptional toxicity of heavy metals, their prevalence and consistency (Sharma and Bhattacharya, 2017).

The contaminants that can be found in drinking water are biological pollutants (toxins, NOM and microorganisms) and heavy metals. Many studies have shown that carbon nanotubes (CNTs) require better adsorption of biological pollutants and heavy metals compared to the use of conventional water purification technologies (Barakat, 2011; Das *et al.*, 2014b). Potential application of CNTs in water/wastewater treatment due to their high specific surface area, strong antimicrobial activity, low toxicity, chemical stability etc. is in the area of adsorption, disinfection and membranes (filters) (Amin *et al.*, 2014). The biggest threats to water and environment are heavy metals, which fall into the most dangerous pollutants because they are toxic at low concentrations, are not biodegradable, have the ability to accumulate in living organisms and thus reach the food chain (Milasinovic *et al.*, 2016). Also, in many developing country, wastewater from households and industry is discharged without or with minimal treatment (Šušteršič *et al.*, 2018). The inorganic pollutants such as arsenic (As) (Petrusevski *et al.*, 2007; Veličković *et al.*, 2013) and heavy metals (lead (Pb) (Brooks *et al.*, 2010; Veličković *et al.*, 2013), zinc (Zn) (Ali *et al.*, 2019b), copper (Cu) (Roy and Bhattacharya, 2015), cadmium (Cd) (Ihsanullah *et al.*, 2017), chromium (Cr) (Sharma *et al.*, 2009; Roy and Bhattacharya, 2015), nickel (Ni) (Mansour and Hasieb, 2012), mercury (Hg) (Homayoon *et al.*, 2017)) come from various industries (Ali *et al.*, 2019a; Das *et al.*, 2014a; Roy and Bhattacharya, 2015). Functionalized CNTs are therefore used as adsorbents for the removal of these pollutants because of the many advantages they possess, as well as the functionalized CNT membranes.

The World Health Organization (WHO) has identified arsenic, cadmium and lead as particularly harmful to human health. According to the recommendations of the World Health Organization, the maximum permissible concentration of these metals (mg L^{-1}) in drinking water for arsenic is limited to 0.01, for cadmium to 0.003 and for lead up to 0.01. Some of this elements listed in Table 3.

Arsenic is usually regarded as a hazardous heavy metal even though it is actually a semi-metal (Barakat, 2011). The presence of arsenic in drinking water, even at extremely high concentrations, does not cause a change in the taste of the odor, color or appearance of water. Therefore, the presence of arsenic in drinking water can be determined only by relatively complicated analyses.

The range of arsenic concentrations found in nature is wide (in natural waters of 0.5 up to 5000 $\mu\text{g L}^{-1}$, in the rocks of 500–2500 $\mu\text{g kg}^{-1}$) (Petrusevski *et al.*, 2007). Arsenic is present in nature in organic and inorganic compounds in various valence states (-3 , 0 , $+3$, $+5$). It is relatively mobile and it can be found in traces in many materials. In Europe, there are also areas with relatively high concentrations of arsenic in groundwater used for water supply. The most vulnerable are: Turkey (10,700 ppb), Czech Republic (1690 ppb), Italy in volcanic areas (1558 ppb), Finland (1040 ppb), Hungary (800 ppb), Spain (615 ppb), Croatia (610 ppb), Switzerland (370 ppb), Romania (200 ppb), Serbia (150 ppb) (Budimirović *et al.*, 2017). There are numerous techniques for removing arsenic from the water (adsorption, coagulation and flocculation, precipitation, ion exchange and membrane filtration), but none can solve all the problems that appear in practice, because each of them has its advantages and disadvantages. Alternative methods such as ozone oxidation, bioremediation, and electrochemical treatment (Jame and Zhou, 2016) are also used, but these procedures require detailed research into widespread use in arsenic removal systems. The method that will be used depends on a number of factors: initial concentration and appearance of metals, water composition – presence of co-existing ions and their impact on arsenic removal, local standards for drinking water, required plant capacity, investment costs, operating costs of the plant, impact on the environment, etc.

Budimirović *et al.* (2017) analyzed removing As(V) , Pb^{2+} , and Cd^{2+} with the multi-wall carbon nanotubes (MWCNTs) modified with polyamidoamine dendrimers from natural water. The authors proved that the introduction of a large number of reactive amino groups repeatedly increases the power of CNTs adsorption of pollutants cations found in water. By the additional deposition of various forms of iron onto the adsorbent, an exceptional adsorbent for the removal of arsenic ions is obtained.

The high use of lead and cadmium in industry has led to the presence of these metals in all environmental media. Since they can all be found in air, water and soil, they easily enter the food chain and biological systems. When they reach the human body, they bind to erythrocytes and thus spread throughout the body. They are mostly accumulated in the bones, liver, kidneys and nerve tissue, and are excreted mainly in the urine. They are extremely harmful to the brain and nervous system.

Table 3 Possibility of using CNT for removal of heavy metals ions

<i>Heavy metals ions</i>						
<i>Contaminats</i>	<i>Conventional technique</i>	<i>CNTs adsorbents</i>	<i>Concentration (mg L⁻¹)</i>			<i>Footnote citations</i>
			<i>EU</i>	<i>WHO</i>	<i>US EPA</i>	
Zn ²⁺	Ion exchange, Chemical precipitation, Oxidation, Membrane filtration, Adsorption	Oxidized CNTs f-MWCNTs MWCNT-NH ₂	0.1–5	no value has been proposed	5	^A
As(III) and As(V)	Precipitation, Ion exchange, Oxidation, Nanofiltration, Reverse osmosis, Electrodialysis	MWCNT-NH ₂ MWCNT-ZrO ₂ Iron oxide Coated MWCNTs	0.05	0.01	0.05	^B
Ni ²⁺	Chemical precipitation, chemical oxidation or reduction, Filtration, Ion exchange, Membrane technologies, Electrocoagulation (for wastewater)	Oxidized CNTs MWCNTs MWCNTs/iron oxide Oxidized MWCNTs	0.05	0.07	0.04	^C
Cd ²⁺	Adsorption, Electrocoagulation (for wastewater)	CNT-COO — CNT-KMnO ₄ CNT-HNO ₃ MWCNT-NH ₂ MWCNT-HNO ₃ Oxidized MWCNTs	0.005	0.003	0.005	^D
Cu ²⁺	Chemical precipitation, Electrocoagulation (for wastewater)	CNT-OH MWCNT-NH ₂ Oxidized MWCNTs	0.1–3	2	1	^E
Pb ²⁺	Chemical precipitation, Adsorption, Ion exchange Filtration Reverse osmosis	CNT CNT-HNO ₃ MWCNT-NH ₂ MWCNT-HNO ₃ Acidified MWCNT MWCNT/Fe ₃ O ₄	0.05	0.01	0.015	^F

^AAli *et al.* (2019b); Lu and Chui (2006).^BVeličković *et al.* (2013).^{C, D, E}Anitha *et al.* (2016); Fu and Wang (2011); Mansour and Hasieb (2012); Pandey *et al.* (2007); Rahman *et al.* (2019); Un and Ocal (2015); Zhu *et al.* (2019).^FBiela and Šopíková (2017); Brooks *et al.* (2010).

In some papers researchers analyzed the possibility of removing cadmium (Ihsanullah *et al.*, 2017), lead (Li *et al.*, 2007), zinc (Ali *et al.*, 2019b), and arsenic from wastewater with CNTs. Li *et al.* (2007) used multi-wall carbon nanotubes (MWCNTs) functionalized with amino polyethylene glycol (PEG) for removing cadmium and lead. Tofighy and Mohammadi (2011) reported that adsorption capacity onto the oxidized CNT sheets have been ordered as $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ and depend of nature and concentration of acidic functional groups. Pendergast and Hoek (2011) showed that alumina nanoparticles are useful as adsorbents for nickel (Ni^{2+}) in aqueous solutions. Ihsanullah *et al.* (2017) impregnated the surfaces of the CNTs with 1%, 10%, and 20% of Al_2O_3 nanoparticles in order to remove the cadmium. The maximum removal rate of 84% was achieved at 10% of Al_2O_3 . In the paper by Ali *et al.* (2019b) the removal percentage of different pollutants in Ar/O_2 plasma treated MWCNTs membrane in the wastewater effluent has been ordered as $\text{Mn}^{2+} > \text{Fe}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+} > \text{Na}^+$ and is higher than pristine CNTs.

In 2017, EU adopted Regulation on mercury, which covers the full life cycle of mercury. Levels of mercury in groundwater and surface water are less than $0.5 \mu\text{g L}^{-1}$ (WHO). The U.S. EPA has determined that mercury in water can cause kidney damage due to short-term exposure at levels above the maximum contaminant level. Many authors analyzed the possibility to remove mercury with MWCNTs, using different temperatures, pH and contact time. In the paper by Homayoon *et al.* (2017), authors described how MWCNTs was functionalized by treating them with thiosemicarbazide to make their large surface areas attract mercury.

Also, many researchers analyzed the possibility to remove biological contaminants. CNTs have shown a great antimicrobial characteristics. Zhu *et al.* (2019) has proven that mullite-CNTs composite membrane eliminated bacteria such as *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) from drinking water. Jame and Zhou (2016) reported that electrochemically CNT-based treatment systems have been very effective for removing different chemical and biological contaminants with efficiency higher than 90%.

One of important parameters that the researchers analyzed is the impact of pH on the removal efficiency of heavy metals, microorganisms and salts. Researchers found that efficiency is strongly pH dependent, and at pH of 7–10, the functionalized CNTs were most effective adsorbents of different contaminants (as a zinc, cobalt, cadmium, leads, nickel, chromium etc.) (Ali *et al.*, 2019a,b; Santhosh *et al.*, 2016). Veličković *et al.* (2013) concluded that adsorption of Cd(II), Pb(II) and As(V) strongly depends on pH and was found that the optimal pH was 8 for Cd^{2+} , 6 for Pb^{2+} and 4 for As(V). Lu and Chui (2005) have shown that the adsorption capacity of Zn^{2+} onto CNTs increased with the increase in the pH range of 1–8, and decreased at a pH of 12. In addition to heavy metals, dyes of wastewater also represent a big problem, because of their high toxicity and must be removed before discharge into the environment (Fard *et al.*, 2018). They usually come from industry and techniques for removing them from wastewater are adsorption, ion exchange, inverse osmosis, coagulation and flocculation, biologic processes, chemical deposition, and advanced oxidation processes (Ali *et al.*, 2019a; Fard *et al.*, 2018). Fard *et al.* (2018) used MWCNTs for removal of Direct Blue 71 and showed that the maximum amount of dye was observed at $\text{pH} = 3$.

When the impurities are removed, the membranes are fouling. The membrane fouling is very important and universal problem, because it causes degradation of membrane characteristics. It is caused by the accumulation of inorganic salts, solids (particles or colloids) and dissolved organic in the membrane matrices (Ali *et al.*, 2019a,b). Numerous studies have shown that f-CNT membranes have better anti-fouling properties. Celik *et al.* (2011) analyzed multi-walled carbon nanotube/polyethersulfone (C/P) blend membranes and their anti-fouling efficiency. They found that 2% of MWCNTs membranes significantly decreased fouling caused by natural water.

Legislation and Regulatory Framework of Nanotechnology

Between 2001 and 2014, over sixty countries from Europe, Japan, Russia, China, Brazil, and India have established nanotechnology initiatives (Clunan *et al.*, 2014). In 2004, the US Environmental Protection Agency (EPA) identified the needs for the environmental applications of CNTs for remediation or treatment (US EPA, 2007; Tofighy and Mohammadi, 2011). China was among the first countries to adopt regulations and a large number of national standards for nanosecurity and also was the first to establish its United Working Group for Nanomaterials standardization in December 2003 (Karim, 2013). Also, Republic of South Korea established the inter-ministerial “National Nano-safety Strategic Plan (2012–2016)” and Japanese Ministry of Health, Labor and Welfare on 2009 implemented Notification on Precautionary Measures for Prevention of Exposure etc. to Nanomaterials (Schulte *et al.*, 2014). In 2006, South Africa has developed its National Strategy for Nanotechnology, and has established innovation centres that are focusing on water treatment.

European Commission (EC) recommended the definition of nanomaterial in 2011 and one of European legislations that concerns the nanomaterials is Regulation (EC) No 1907/2006 of the Parliament and of the Council of the European Union called Registration, Evaluation and Authorization of Chemicals (REACH). Every five years, the European Commission publishes and adopts “Review of REACH”. In December 2018, the Commission adopted Commission Regulation (EU) 2018/1881 to modify REACH Annexes I, III, and VI–XII, introducing nano-specific clarifications and new provisions in the chemical safety assessment (Annex I), registration information requirements (Annex III and VI–XI) and downstream user obligations (Annex XII). For now, there is no single definition of nanomaterials and it is very difficult to establish national, and even harder, international standards, which represent the base of the nanotechnology regulations. As a result, countries are implementing different approaches based on national regulations of nanotechnology.

Park *et al.* (2016) in its research reported that the global production of carbon nanotubes is estimated at 350 tones/year and that there is no regulation for controlling the discharge of these materials into the environment. With the development and

commercialization of nanomaterials, potential harmful effects on human health are increasing. Although nanotechnology has proven to be very effective in different areas, there is still not enough information regarding the impact on the environment and human health. Nanoparticles are expected to be found in aquatic systems as a result of unintentional discharge during any phase of their life cycle. The problems and risks that may arise after production and application of nanomaterials have led to the establishment of numerous documentation and projects by ISO Technical Committees (ISO/TC) 229 related to toxicological effects of nanomaterials.

Toxicity of CNTs

Many industries such as painting, electronics, optics, cosmetics, energy and production of catalysts emitted nanoparticles (silica, titanium, Al, Fe and Zn) to landfills, soil, water and atmosphere (Keller *et al.*, 2013). When the use of CNTs is intensified, increasing attention is being paid to cause toxicity trials, ways of overcoming the toxic properties of CNTs and their safe use.

Because of CNTs similarity in size and shape with asbestos fibers, they represent a potential risk to human health and the environment. Not all CNTs are toxic, and also by changing the shape, size, purity, production method and functionalization, CNTs toxicity can be decreased. It has been concluded that higher toxicity is observed with a longer length and larger diameters of CNTs (Madani *et al.*, 2013). CNTs can enter through the gastrointestinal tract, with inhalation to the respiratory system (Kobayashi *et al.*, 2017), through the skin and blood.

When it comes to treatment of drinking water and wastewater water, nanotechnologies have shown very high efficiencies in removing pollutants, but their toxicity remains questionable (Werkneh and Rene, 2019). Using CNTs, almost all three types of pollutants, i.e., organic, inorganic and biological pollutants can be removed (Upadhyayula *et al.*, 2009). CNTs are a popular adsorbent and are required in high volumes for adsorbing water pollutants of extremely high concentrations (Das *et al.*, 2018). Pristine CNTs are themselves problematic because of their generic impurities such as metals and carbonaceous agents that pose nanosafety issues. Adsorbing water pollutants changes the CNT characteristics such as pore size and volume, surface charge or energy, stability, hydrophobicity and functionalities (Das *et al.*, 2018).

After wastewater treatment, pollutants, like residual aluminum salts and iron can still be found in the wastewater. For example, some research concluded that aluminum salts may cause Alzheimer's disease; and increased levels of iron in the body above the World Health Organization (WHO) limit levels can increase the risk of a variety of diseases including cancer, vascular diseases, and neurological disorder conditions (Simate *et al.*, 2012). In many cases, studies that analyze the effects of CNTs on the human health and the environment, examine very little the physical properties of CNTs and their impact on behavior of CNTs in the environment. Without the systematic physical characterization of each type of examined CNTs, the assessment of the possible risks, caused by attendance of CNTs in environmental are unimaginable.

Conclusion

Water is an inevitable and very important factor of socio-economic development of each country. Water resources are becoming a deficient resource on a global scale level. Water requirements grow rapidly due to anthropogenic factors: an increase in world population, increased volume of economic development, as well as climate change.

Nanotechnology can improve water treatment because the surface area is larger, contact with water is improved; CNTs possess high reactivity; fast kinetics; specificity contaminants and with the development of new nanomaterials the cost is reduced. However, some obstacles still exist to bring the CNTs into the mass production. One of them is a complicated method for the synthesis of CNTs, as well as obtaining smaller pores size and diameter for CNTs membranes. Also, very important barrier to mass production is their cost in water/wastewater treatment, as well as the still under-tested impact on human health and the environment.

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Further Reading

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Application of Bioceramics in Ophthalmology

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Introduction

Bioceramics are the special ceramic materials that are specially designed for the repair and reconstruction of the body parts that are damaged or diseased. The use of Ceramic Matrix Composites (CMCs) was initially directed to the repair of hard tissues, such as bone and teeth, but later they have been also applied in other medical areas like ophthalmic surgery ([Gerhardt and Boccaccini, 2010](#); [Rahaman et al., 2011](#); [Juhasz and Best, 2012](#)).

The use of ceramics in ocular surgery began from the 18th century, and since then, the different bioceramics have been investigated and used in ocular surgery ([Pellier de Quengsy, 1789–1790](#)). Bioceramics have a great potential in ophthalmic surgery due to a set of unique properties that can be properly and successfully exploited for ocular applications. These materials were tested and applied in three different fields of ophthalmic surgery: oculoplastic surgery for orbital floor repair, orbital implants for anophthalmic patients and ocular keratoprosthesis (artificial cornea).

Currently, Hydroxyapatite (HA), Polyethylene (PE) and Alumina are the most used biomaterials for ocular surgery. Recently, many others biomaterials, among them Bioactive glasses (BGs) and Bioactive glass-ceramics (BGCs), have been extensively investigated for applications in ocular surgery. The extraordinary versatility of these biomaterials, which primarily depends on the flexibility of their composition, allows various applications in ophthalmology.

Orbital Floor Repair

In facial trauma, the orbital floor, which is extremely thin (below 0.50 mm), is the most common site of bone fracture ([Chang and Monolidis, 2005](#)). That can cause herniation of the orbital contents into the maxillary sinus set underneath. Surgical intervention is substantial for the restoration of the original anatomical orbit structure ([Shin et al., 2013](#)). It is very important to provide support to the orbital cavity and avoid major complications such as extraocular movement limitation, double vision (diplopia), and recession of the eyeball within the orbit (enophthalmos). The implant acts as a bone graft providing structural support at the bone defect site (fracture) and it is often designed as a porous scaffold to promote bone in-growth and a safe anchorage to surrounding host tissues ([Baino, 2011](#)). In the case of orbital floor repair, the implant solubility must be compatible with bone healing rate.

Implants for the orbital floor, or for its anatomical reconstruction to be more precise, have been manufactured out of broad range of various materials. They may be categorized as autogenous, allogenic and alloplastic (artificial) ([Mok et al., 2004](#)). Autogenous implants (i.e., the transplant of tissue from the same individual) include grafts of bone, cartilage, and fascia lata. Autologous bone graft allows full integration of the material once it is implanted and it is usually the preferred option to repair the defect. Allografts (i.e., the transplant of tissue from one individual to another of the same species, including those from cadaveric donors) are an alternative option to auto-grafts.

Synthetic materials have been introduced to reduce some limitations of autologous grafts (especially because it carries the need of additional surgery in the same patient). The ones that are most commonly used are: porous hydroxyapatite (HA) and polyethylene (PE). Because of their open-pore structure vascularization, bone ingrowth and soft tissue are enhanced which stabilize the implant in the defect and exclude the necessity for the use of fixation screws and sutures. However, those implants do not have osteoinductive properties i.e., do not induce new bone in-growth, their fragile nature i.e., their brittleness (especially of HA) and high infection rate (especially of PE) make these implants less attractive compared to autologous bone grafts ([Villarreal et al., 2002](#)).

Orbital Implants

Severe eye diseases such as malignant intraocular and infraorbital tumors, painful blind eyes, severe intraocular infections or eye damages caused by trauma all lead to the physical removal of the natural eye. When the removal of the diseased eye is performed (through the processes of enucleation or evisceration), an orbital implant is inserted into the patient's anophthalmic socket in the same position as the eye in order to provide adequate volume. There are two ways that the extraocular muscles can be attached onto the implant during the operation: directly to the implant and indirectly, by suturing extraocular muscles to the wrapping material over the implant, thus providing maximum motility of the implant. Soon afterward, the anterior tissues i.e., Tenon's capsule and conjunctiva are closed over the implant. With the aim of achieving good esthetic appearance, ocular esthetic prosthesis could be fitted over the orbital implant.

The adequate orbital implant must be biocompatible with orbital tissues and nondegradable i.e., must be permanent in order to ensure appropriate volume replacement for the patient's lifetime without undergoing volume loss.

Most commonly used materials for orbital implants manufacturing are PE (polyethylene), Porous HA and alumina. These materials consist of an interconnected microporous network that allows them to play a role as a passive framework for fibrovascular tissue penetration, and that is helpful when anchoring mechanically the implant to the soft orbital tissues (Chalasani *et al.*, 2007).

Artificial Cornea (Keratoprosthesis)

Keratoplasty (corneal transplants from donor eyes) is a procedure that removes and replaces a damaged cornea with donor tissue. In succession to the repeated transplanted graft failure, the only possible course for restoring vision is the replacement of a highly damaged cornea with a keratoprosthesis (artificial cornea).

The artificial cornea is made of two parts. The first part is a transparent optical core transmitting light into the eye. The second part is a peripheral rim generally known as keratoprosthesis “skirt” which fixes the implant to the recipient cornea.

The artificial cornea that can be considered ideal should consist of materials that encourage integration with the corneal epithelium, stroma and endothelium since epithelial layer serves as a barrier to infection, while stromal anchorage makes better the retention of the prosthesis. In addition, the materials should manifest adequate permeability for nutrients and fluids (Gomaa *et al.*, 2010).

Nowadays, the implanted keratoprosthesis are mainly made of inert polymeric materials. There are different possibilities aimed at creating better biointegration of the device in the host corneal tissue, and Strampelli’s osteo-odonto-keratoprosthesis (OOKP) is among them. The procedure involves the usage of a canine tooth and surrounding alveolar bone (harvested from the patient) to act as a carrier for a PMMA optical lens (Strampelli, 1963). Bone and tooth show biocompatibility in the ocular environment, but in the course of time, the dentine frame is subjected to partial resorption which can cause loosening of the optical core and finally prosthesis loss (Ricci *et al.*, 1992). This issue was the most significant reason why synthetic alternatives to the tooth-derived skirt of OOKP have been proposed, including BGs-based materials (Huhtinen *et al.*, 2013).

Hydroxyapatite (HA)

Hydroxyapatite (HA) are porous bioceramics. Different researches were conducted to determine their possible use for orbital floor repair and manufacturing of orbital implants. At first, they were bone-derived. That means that they were prepared by thermally treating spheres of bone to destruct all organic matter, leaving only the Calcium orthophosphates (CaPs) mineral framework that was predominantly constituted by ultra-microscopic crystals of HA. Nevertheless, bone derived HA implants are more expensive, and they are not mechanically strong because of high porosity than the analogous devices made of HA from other sources. Due to that, natural sea coral has been used to create coralline porous HA sphere for orbital floor repair and porous orbital implants after evisceration/enucleation surgery. Since the structure of coralline HA is porous, that makes possible host fibrovascular in-growth which possibly decreases the risk of implant extrusion and bacterial colonization on the prosthesis device surface (Nunnery *et al.*, 1993). Perry introduced Coralline porous HA sphere in the 1980s (Bio-Eye®) as an orbital implant by Perry (1991). However, Bio-Eye® had an uneven surface which could create issues such as the abrasion of the thin conjunctiva and Tenon’s capsule, subsequently leading to the implant extrusion. Synthetic HA has been suggested as a less expensive material for orbital bone reconstruction and orbital implant.

In regards to the orbital bone reconstruction, making use of the data gained by micro CT or MRI derived files, by the computer-aided design, commercially available artificial HA were used to create 3-D porous implants for orbital floor repair for each individual patient. This manufacturing system could create scaffolds perfectly fitting the required anatomical dimensions. In cases of orbital floor repair, the size of the porous plates can reproduce the contour of the bone fracture (Lemke and Kikkawa, 1999). This kind of manufacturing system was also successfully employed for the creation of HA porous orbital implants and the porous skirt of synthetic keratoprosthesis. By doing this the orbital implant volume can be properly adapted to be suitable to the individual eye socket, and the porous skirt of synthetic OOKP could be tailored in accordance with the characteristics of each patient’s eye (Levy *et al.*, 1997).

This type of synthetic custom-made HA scaffolds is an excellent alternative to autologous grafts and polymeric materials in orbital floor surgery. Nevertheless, synthetic HA are very brittle which could cause intraoperative difficulty of implantation and postoperative loss of structural and mechanical integrity (Elmazar *et al.*, 2003).

Regarding craniofacial reconstruction HA can be combined with carbonated apatite to produce moldable pastes, more widely known as “bone cements”. When water reaches salts, they react and create a dense paste that could then be shaped intraoperatively. Mathur *et al.* (2003) reviewed the usage of HA cements considering cranio-maxillofacial surgery, involving orbital floor repair.

In the mid-1990s, FCI3, i.e., synthetic HA orbital implants were used in the clinical practice in the area of anophthalmic surgery, (Jordan and Bawazeer, 2001). Such implants had the chemical structure analogous to that of Bio-Eye®. Yet, there are some architectural differences between them, involving lower overall porosity of FCI3 implants in comparison to Bio-Eye® (Mawn *et al.*, 1998).

HA was used as well for producing composite implants for anophthalmic ocular surgery and orbital floor reconstruction. HA/PE (Polyethylene) composite implants have been marketed and known as HAPEXTM more than 20 years and successfully

adopted as a bone replacement material in otolaryngology (middle ear bone prostheses) (Meijer *et al.*, 2002) and orbital floor repair (Tanner, 2010). The combination of stiff but brittle HA with low-modulus, tough and bioinert PE exerts attractive properties for bone substitution (Zhang *et al.*, 2007).

Various researchers have conducted experiments with the usage of HA as a coating material on porous orbital implants and solid polymeric or carbon substrates for keratoprosthesis. A group of researchers from Korea has produced and tested a synthetic HA-coated porous alumina eye implant in the early 2000s; the porous alumina skeleton serves as a load bearing structure, whereas the HA coating layer that is 20- μ m thick was supposed to ensure higher biocompatibility and long-term stability in the ocular orbit (You *et al.*, 2003). Concerning the area of artificial cornea, Sandeman *et al.* proposed the usage of porous carbon for OOKP in combination with a HA coating (Sandeman *et al.*, 2009). In other respects, carbon was the first proposed ceramic material for the production of a peripheral porous skirt to firmly anchor the keratoprosthesis to host tissue. HA coating substantially increased keratocyte adhesion to the carbon mesh. Wang *et al.* conducted experiment in 2011 to evaluate whether the HA coating on model PMMA substrates (which is the major constituent of the keratoprosthesis) can make keratocytes proliferation better compared to unmodified PMMA surfaces; the researchers came to a conclusion that HA coating did, in fact, induce an enhancement of keratocyte proliferation in comparison to unmodified PMMA surfaces (Wang *et al.*, 2011). Synthetic HA was also proposed as a new, promising material for the porous skirt of keratoprosthesis (Mehta *et al.*, 2005).

Titanium oxide (TiO₂) can be the alternative material to HA. Titanium oxide is a synthetic bioinert material that was researched for usage in corneal surgery for keratoprosthetic porous skirt. In comparison to HA, TiO₂ highly improved keratocyte proliferation and tissue integration and decreased device failure rates during keratoprosthesis surgery (Tan *et al.*, 2012).

Alumina

Alumina is bioinert ceramic material mainly used in the ophthalmic surgery for the production of porous orbital implants and keratoprotheses.

Since the late 1990s, porous alumina was suggested to manufacture orbital implants for oculoplastic surgery; this kind of material was approved in 2000 by US Food and Drug Administration (FDA) and has been marketed as "Bioceramic implant". Jordan *et al.* (2000) have compared alumina and coralline HA orbital implants in an experiment conducted on rabbits. As a result of these studies authors have concluded that the alumina and HA implant had equal biocompatibility, but that HA wasn't less expensive. Another argument concerning the proliferation of orbital fibroblasts in favor of alumina was made by, Mawn *et al.* (2001) who have assessed that cell proliferation was better on alumina than on coralline and synthetic HA. In addition to that, the fibroblasts on the Bio-Eye[®] and FCI3 implants both had debris associated with them, whilst the alumina implant did not have any of these debris, which was primarily attributed to alumina's fine crystalline microstructure. Jordan *et al.* were the first to report outcomes of Bioceramic implant in humans in 2003 (107 patients over a 3-year follow-up) (Jordan *et al.*, 2003); the researchers reported that alumina orbital implant had more favorable characteristics in comparison to the coralline HA porous sphere, which is commonly known as the "gold standard" reference (e.g., lower tendency to extrusion due to a smoother surface).

Polack and Heimke (1980) designed an artificial cornea in 1980, made out of an alumina plate with a 3-mm central perforation with an optical cylinder (60 diopters of power) threaded to it. Experimental studies in human patients indicated that soft tissue attached to the surface of the material prevents its extrusion and surface epithelial in-growth in anterior chamber. Approximately a decade later, Caldwell and Jacob-LaBarre making comparison between alumina and HA, reported that the bacterial adhesion on alumina surface was lower than that on HA substrates, but otherwise the average keratocyte adhesion strength on alumina disks was lower than that on HA (Caldwell and Jacob-LaBarre, 1989).

Glass

Optical glasses have been used for a long time to correct refractive anomalies and to increase visual acuity. In the 18th century, Venetian glassmakers start producing prosthetic human eyes that were fragile thin glass shells, with poor fit and little comfort (Fechner and Fechner, 1979). Mules described the surgical procedure in which a hollow glass sphere is placed into an eviscerated globe in 1885 (Mules, 1885). However, the extrusion rates were high in orbital implants cases (50%–90%). Glass ocular prostheses as well as glass orbital implants were prevalently used until WWII, when they got replaced by PMMA devices (Gougelmann, 1970).

Glass was the first material for keratoprosthesis since it is transparent. In the 18th century Pellier de Quengsy proposed an artificial cornea consisting of thin silver-rimmed convex glass disk as a keratoprosthesis (Pellier de Quengsy, 1789–1790). Since then, glass was proposed as a key component of an implantable device. In the 19th century Abate made an attempt to make a skirt around the glass optical core, for the purpose of promoting a better incorporation of the prosthesis into the patient's cornea (Friend, 1983). With this aim he created a keratoprosthesis made of a glass disk surrounded by a skirt that consisted of natural polymers: the device was implanted in dog and cat corneas. This skirt underwent fast degradation and keratoprosthesis was extruded in 1 week. Over the 20th century, the usage of glass was abandoned because of the advent of synthetic polymers for corneal implants and the increasing attention towards donor corneal transplants.

Bioactive Glasses (BGs) and Glass-Ceramics (BGCs)

From 1969–1971, Hench and his coworkers created and examined various glass formulations based on the SiO_2 – Na_2O – CaO – P_2O_5 oxide system, and they finally selected the composition 45 SiO_2 –24.5 Na_2O –24.5 CaO –6 P_2O_5 (wt%), characterized by high amounts of Na_2O and CaO , as well as a relatively high $\text{CaO}/\text{P}_2\text{O}_5$ ratio that makes the surface of the material extremely reactive in physiological environment of the host (Hench *et al.*, 1972; Hench, 1998, 2006). This glass composition was originally referred to as 45S5 and was shortly after trademarked by the University of Florida under the name of Bioglass®.

Bioactive glasses (BGs) and glass-ceramics (BGCs) are special type of bioceramics and they have particular ability to stimulate cell activity and tissue regeneration *in vivo*. Over the years, these materials have been researched in the shape of dense implants, powders or porous scaffolds by different researchers worldwide especially for the purposes of applying them in orthopedic and dental surgery (Baino, 2011; Chang and Monolidis, 2005; Gerhardt and Boccaccini, 2010). BGs are able of creating a bone-like hydroxyapatite layer on the surface when it is put in contact with bodily fluids. The creation of a surface apatite layer after contact with biological fluids is the main goal. Hydroxyapatite is the main mineral of natural bone tissue, BGs are an important factor in a stronger attachment to the host bone. In this manner, they could bond tightly to bone making stable interface (osteoconduction). Under other circumstances, they are capable of stimulating new bone growth and self-repair (osteoinduction) and of accelerating tissue healing kinetics and bond to soft tissues (Hench, 2009).

BGs and BGCs have been researched with the aim of bone and dental repair. The bioactive glasses and glass-ceramics have proved to be suitable substances for applications in eye surgery. BGs and BGCs can make better the performance of ocular implants. Bioactive glasses are a very promising in this field of orbital floor fractures and defect repairment because they are known to bond both to bone and muscle tissue which is the main property for implants used in reconstructive surgery. Furthermore, through the release of adequate ionic dissolution products, porous bioactive glasses can stimulate angiogenesis and fibrovascular in-growth, which are significant to ensure a suitable motility of orbital implants and lower the risk of infections. It was discovered that porous bioactive glasses are able to stimulate the fibroblasts adhesion and proliferation, and that ability made them a material that is potentially desirable and a leading candidate for a new, smart generation of keratoprosthesis (Baino and Vitale-Brovarone, 2014; Baino, 2015; Baino *et al.*, 2018).

BGs and BGCs in Orbital Floor Repair

Several researchers have used S53P4 glass with oxide weight composition 53% SiO_2 , 23% Na_2O , 20% CaO , and 4% P_2O_5 for the repair of orbital bone fracture (Kinnunen *et al.*, 2000; Aitasalo *et al.*, 2001). Based on the data reported in above mentioned studies, BG plates promise to be reliable solution for reconstruction of the orbital floor, for S53P4 glass is biocompatible, bioactive (meaning it stimulates new bone growth) and also biodegradable at a slow pace (thus providing adequate structural support during bone regeneration period). The silicate bioactive glass S53P4 makes better implant biointegration that is important for a successful clinical outcome. Besides, tomographic scanning qualitatively showed new bone growth surrounding the implanted BG. The results of these studies emphasize the adequacy of the bioactive glass S53P4 for orbital floor fracture repair, which can be a promising alternative to conventional autologous implants. Through stimulation of patient's own tissue, bioactive glass provides a healing-promoting environment, leading to biological fixation of the prosthetic element and decreasing the incidence of extrusion. This efficiently removes the need for invasive screws or threading to fix implants in place.

Generally speaking, BGs and BGCs have a good mechanical compatibility with the orbital bone. Nevertheless, they have several limitations: they have high brittleness and rigidity and because of that they could not be shaped and molded during operation. With the aim of resolving this problem, Peltola *et al.* (2008) developed a set of stainless-steel templates to guide the selection of the correct glass plates that it almost perfectly fitted the surrounding orbit bone defect margins and anatomy. The selection of the adequate plate size and shape compatible with the dimensions of the bone defect allowed the correct definition of the implant design to adequately cover the structural defect so mechanical fixation (the use of screws) was no longer necessary.

BGs in the powder form can be used to produce 3-D porous scaffolds in various sizes, shapes, with different pore architecture and mechanical properties. As mentioned above, this technique was already successfully applied for the creation of HA porous implants for oculoplastic surgery (Levy *et al.*, 1997). Considering the usage of micro CT or MRI-derived files as input data for CAD/CAM manufacturing systems it is possible to create scaffolds exactly fitting the needed anatomical dimensions.

BGs and BGCs in Orbital Implants

The use of stiff orbital implants is advantageous during the operation since the surgeon can easily maneuver and position the implant into the orbital cavity. Nevertheless, there are disadvantages to the existing orbital implants that include the risk of migration and extrusion, postoperative infections as well as low motility (Chalasanani *et al.*, 2007). However, a mismatch in stiffness between eye implant and the soft tissue surrounding it, combined with the repetitive movement of the prosthesis may cause the erosion of the conjunctiva which covers the front of the implant and the consequent implant exposure.

BGs and BGCs could prevail over those issues, and further enlarge the performance of ocular implants. These materials are efficient considering angiogenesis and fibrovascularization i.e., stimulating fibrovascular in-growth, and thus they can show good potential in promoting healing of soft tissue surrounding the implant. This is the most important characteristic to ensure an adequate

motility of orbital implants as well as minimizing most common postoperative complications of orbital implantation surgery like exposure and migration and. Appropriate structure of BG composition can enhance implant material angiogenic characteristics, thus for increasing the fibrovascular in-growth, which represents the most important added value for ocular prosthesis.

Xu *et al.* (1997b) implanted BGC porous orbital implants in enucleated rabbits to evaluate their biocompatibility. During 6-month postoperative follow-up examiners observed no rejection while ultrasound examination and histological analysis indicated significant fibrovascular in-growth into the implant. These results gave the encouragement to the same authors to implant the BGC orbital implants in 102 human patients, an endeavor that had success rate of 96.1% (Xu *et al.*, 1997a). There was a study, conducted by Brandao *et al.* (2012) in which they placed 45S5 Bioglass[®] and Biosilicate[®] non-porous cone implants in rabbit orbital cavities in order to evaluate their biocompatibility. The study showed that 45S5 Bioglass[®] and Biosilicate[®] implants do not provoke the orbit infection or fluid accumulation and the implants proved capable of bonding to soft tissues.

Various silicate bioactive glass and glass-ceramic compositions have been suggested for manufacturing orbital implants with the aim to make better their mechanical features (e.g., increase of strength) and bioactivity. Silicate BG and BGC formulations have been used to construct porous orbital implants in the form of single-phase materials or as a second phase added to a polymeric matrix to produce a composite porous implant. Medpor[®]-PlusTM is a commercial example of the orbital implant which is a blend of 45S5 glass and porous PE particles (Novabone[®]) in a 30:7030 ratio. In another way, NovaBone[®] is the trade name of a 45S5 Bioglass[®] particulate which was put on the market in 1999 after it got the approval for repairing bone defects in orthopedic or maxillofacial surgery (Hench *et al.*, 2004). In regards to the ocular surgery, NovaBone[®] was used to coat porous polyethylene prosthesis for enucleation. The most significant premise for the success of the ocular prosthesis the ability of fibrovascularization, or the growth of vascularize connective tissue inside the implant macropores, so the angiogenesis stimulated by BG was a key added value in this application (Xu *et al.*, 1997a). Naik *et al.* (2007) researched the fibrovascular ingrowth of Medpor-Plus implants in comparison with porous PE implants (Medpor) and concluded that BG magnify significantly angiogenesis. In 2011, Ma *et al.* (2011) checked the clinical outcomes of 170 human patients who had porous BG/PE composite orbital implants placed in their eye-sockets. Almost all of patients reviewed (161 cases) were without complications, the implant motility was good overall, and no cases of conjunctival thinning or inflammation were found. The researchers made a conclusion that the porous glass/PE composite orbital implant can be recommended as a safe implant to restore orbital volume.

In 2006, Choi *et al.* (2006) studied on the effect of bioglass particles on the fibrovascular in-growth process in porous PE orbital prosthesis in rabbits, but in this preliminary study the authors came to a conclusion that addition of BG particulate did not substantially enhance the rate of fibrovascular ingrowth into porous PE ocular implants.

BGs and BGCs in Keratoprosthesis

Concerning the use of BGs and BGCs for artificial cornea, it needs to be approached very carefully. As mentioned above, one of the unwanted effects is the resorption of the porous skirt around the optical core that can provoke the loosening of the keratoprosthesis. Various BG compositions were tested for manufacturing of the prosthetic skirt with the goal to enhance device's biointegration in the host tissue. As emphasized by Chirila (2001), it is more desirable that the skirt materials should be hydrophilic with the goal to support the penetration of biological fluids from the subject tissue. This is the first step in the process of the porous skirt biocolonization. BGs and BGCs are capable of exposing hydroxyl groups after contact with aqueous solutions. Porous BGs allow and even stimulate keratocytes adhesion and proliferation. In this manner, they are the promising candidates for the development of a new class of skirt keratoprosthesis. Besides promoting tissue response towards full integration, the use of these biomaterials allows the construction of totally synthetic devices. Thus, the need and complexity of multi-stage surgical techniques are overcome.

In the late 1970s "Ceravital" were BGS formulations suggested to fabricate an anchorage skirt around experimental OOKP (Bigar *et al.*, 1978; Strunz *et al.*, 1978). It was soon noticed that this material had the inclination to progressively dissolve after contact with biological fluids, over time it lost supporting function and the investigations were stopped.

One significant issue concerning the use of keratoprosthesis is the growth of epithelium between the corneal stroma and the prosthesis material into the anterior chamber which could provoke infections, implant extrusion, development of retroprosthetic membrane and secondary glaucoma. In 1996, Linnola *et al.* (1996) investigated the appropriateness of an apatite/wollastonite (A/W) glass-ceramic coating in rabbits' eyes to overcome those problems connected to keratoprosthesis. The investigated devices consisted of a PMMA optical cylinder surrounded by a peripheral rim of titanium either uncoated or coated with a SiO₂-CaO-MgO-P₂O₅-based apatite/wollastonite glass-ceramic. The researchers concluded that the bioactive glass-ceramic was capable of anchoring the prosthesis to the corneal tissue preventing epithelial down-growth from the surface along the implant into the inside of the eye. This material is capable of attaching the prosthesis to the corneal tissue before the epithelium grows inward. Despite this positive effect, material degradation complications were the most significant reason to stop the investigation.

In order to replace the human tooth and bone in OOKP support due to degradation issues, several researchers have investigated the appropriateness of bioactive glass and glass-ceramic formulations for the fabrication of keratoprosthesis skirts. Santos *et al.* (2011) examined a porous phosphate glass hydroxyapatite (GRHA) and analyzed its physicochemical behaviors through several in vitro tests. These materials allow fibrovascularization and tight fixation. The researchers concluded that it was superior compared to materials in the dense form. Additionally, under physiological pH conditions no material degradation was observed and, consequently, the authors made a conclusion that the porous GRHA exhibited outstanding potential deserving further in vivo studies.

Laattala *et al.* (2011) examined the behavior of four different PMMA/bioactive glass composite materials. Particles of 45S5, S53P4, 1-98 and FL107 were incorporated in a PMMA matrix and the resulting composites were then compared on the basis of the glass dissolution. The aim of the study was to examine the glass bioactivity and the surface porosity left behind after glass degradation for new tissue ingrowth, offering good prosthesis fixation. The PMMA matrix, moreover, is a stiff structure that will not suffer from volume loss for the patient's lifetime.

In 2013, Huhtinen *et al.* (2013) examined two experimental silico-borophosphate BGs for their use as an OOKP skirt substitute. In vitro studies have shown that adherent keratocytes have good adhesive potential, as indicated by their characteristic elongated spindle morphology. These preliminary examinations promote the use of porous BG as a synthetic OOKP skirt, even if dissolution of the glass during time might destabilize the OOKP, stressing that a composite system with a stable backbone structure would be needed to keep the optical core in the correct position while the BG chemically dissolved.

BGs and BGCs as Vehicles for the Controlled Release of Biomolecules, Therapeutic Ions and Drugs

The most important added value of BGs and BGCs is their special capability to release adequate ions with the aim of causing a distinctive, desired response in vivo. It has been showed that ionic dissolution products play a very significant role in affecting the biological response of biomedical materials in vitro and in vivo, stimulating cell activity or exerting other adequate functions (e.g., antibacterial effect). Considering this aspect, examiners paid a great attention to BGs due to their adjustable reactivity in the biological environment (Hench, 2009; Hoppe *et al.*, 2011).

During time, many other bioactive glasses compositions have been suggested for innovative biomedical applications. Bioactive glasses can be used as devices for the controlled release of therapeutic ions and therapeutic biomolecules. The BGs potential for the delivery of different therapeutic biomolecules has been thoroughly examined because of the possibility of incorporating both hydrophobic and hydrophilic groups into their structures (Galaraga-Vinueza *et al.*, 2017). All things considered, the addition of therapeutic ions into the BG formulation and their later release after exposure to a physiological environment was supposed to have osteogenic (McEntire *et al.*, 2015), antibacterial (Baino *et al.*, 2016; Jovanovic *et al.*, 2017), anti-inflammatory (Sun *et al.*, 2001; Jovanović *et al.*, 2017) or angiogenic effects (Sola *et al.*, 2011; Petrović *et al.*, 2018).

The "therapeutic effect" of BGs on soft tissues is mostly attributed to enhanced angiogenesis stimulated by the release of ionic dissolution products from the bioactive glass. It has been reported that calcium ions provokes the migration of epidermal cells and plays significant role in the late stage of healing (Baino and Verné, 2017). In vitro experiments have proved that BGs stimulate the release of angiogenic growth factors in fibroblasts, enhance the proliferation of endothelial cells and incentivizes the creation of endothelial tubules (Day, 2005; Leu and Leach, 2008). Also, in vivo results verified the neovascularization of porous BG implanted in rats (Gorustovich *et al.*, 2010; Gerhardt *et al.*, 2011).

BG and BGC compositions can be properly constructed to obtain materials with various degrees of solubility by varying the ratios between the constituent oxides (e.g., SiO₂, P₂O₅, Na₂O and CaO) and/or incorporating additional metal oxides; in this aspect, biocompatible phosphate glasses can propose a wide range of dissolution kinetics (Abou Neel *et al.*, 2009). BGs are described to be capable of exerting their biological effects through releasing therapeutic ions into the environment. Until nowadays, a few elements (e.g., Cu and Ag) have been included into BG formulation for the purposes of improving BGs' osteogenic and angiogenic capacity and also enhancing their bactericidal activity and anti-inflammation properties.

Regarding this, the usage of a Cu-doped mesoporous bioactive glass (Cu-MBG) coating over a porous HA implant was recently suggested. Ye *et al.* (2014) analyzed antibacterial effect of Cu²⁺ released from MBG-coated HA porous orbital implants. The researchers made a conclusion that Cu-MBG-coated porous HA orbital implants are promising in the prevention of implant-related infections.

In addition, it was showed that Cu²⁺ induces migration and proliferation of endothelial cells during in vitro culture, which can provoke an improved fibrovascularization of the orbital implant in vivo. Doping with small amounts of selected ions, e.g., Cu²⁺ (Bührer *et al.*, 2016), could further potentiate the angiogenetic effect of BGs. Copper is known to regulate several factors engaged in angiogenesis like vascular endothelial growth factor (VEGF), angiogenin, fibronectin and fibroblast growth factor (FGF) 1 and 2, which take important part in the initiation (vascular permeabilization and vasodilation), maturation (proliferation of endothelial cells, morphogenesis and migration), and regulation of blood vessel formation (Urso and Maffia, 2015). With that aim Kargozar *et al.* incorporated cobalt (Co²⁺) into the glass structure to stimulate angiogenesis (Kargozar *et al.*, 2016). In another study, Miguez-Pacheco and colleagues assessed the biological effect of adding therapeutic niobium (Nb⁵⁺) ions to 45S5 BG (Miguez-Pacheco *et al.*, 2018). Their results demonstrated an increase in VEGF release as a valuable sign of angiogenesis. Nevertheless, in both cases (cobalt and niobium) was alerted to possible cytotoxic effects of these ions.

BGs can be also created in the shape of mesoporous materials (MBGs with pore size within 2–50 nm) that, hosting anti-inflammatory drugs or antibiotics, could impart an important added value to implantable ocular devices (Arcos and Vallet-Regi, 2010). Before implantation, porous ocular biomaterials are usually soaked by the ophthalmic surgeons into an antibiotic solution. The functionalization of MBG pore walls has been successfully experimented. It has been showed that in aqueous environment silicate BGs and BGCs can expose reactive hydroxyl groups on their surface that can be employed for the grafting of adequate biomolecules to elicit specific therapeutic actions (Chen *et al.*, 2006). Drug release from MBGs would allow a prolonged therapy to be performed. The amount of incorporated drug and the release kinetics could be pre-determined as a function of the mesopores shape and size. Considering possible ophthalmic applications, the idea of grafting distinctive growth factors, like the vascular

endothelial growth factor (VEGF) to enhance vascularization, or drugs to minimize inflammation and infection, can be of high interest in the area of orbital implants. Sol-gel derived MBGs is a special group of silicate materials developed with the goal of becoming fitting carriers for therapeutic biomolecules. Compared to more commonly used BGs, MBGs have higher pore volume, higher specific surface area, and a uniformed pore size, which make them perfect drug delivery systems. Also, the existence of a significant number of Si-OH groups on the mesoporous channels' walls is recognized as a facilitator for efficient drug delivery, since these chemical groups can interact with target biomolecules (Wu and Chang, 2012; Xia and Chang, 2006).

Different strategy to impart added values to biomaterials is the deposition of a coating on the implant surface. Regarding this, Bains *et al.* (2012) suggested the application of an antibacterial oxide-based composite film on the surface of orbital implants and ocular prostheses. The coating thickness could be modulated from 10 nm to 1 μ m. With that aim silver nanocluster/silica glass composite coatings have been applied on the surface of PMMA orbital implants (Bains *et al.*, 2016), and the material elicited a potent antibacterial effect in vitro due to the release of silver ions for 1 month.

The conclusion was made that two features of BGs determined drug delivery: the dissolution rates and surface characteristics of the glasses. Glass biodegradation in biological environments varies depending on its structure which has a direct effect on the amount of drug released. BG and BGC compositions can be properly constructed to obtain materials with various degrees of solubility. As it was stated, by varying the ratios between the constituent oxides, is possible to obtain BG and BGC materials with various degrees of solubility through modifying the glass composition. This was tested by Kim and colleagues who were able to control the degradation and regulate the drug-release rate of vancomycin from phosphate glass fiber/polycaprolactone composites (Kim *et al.*, 2005). The results of their experiments suggested that the drug release from the composites was greatly determined by the dissolution rates of the materials used, which was mostly related to the glass composition. A very versatile way to impart special properties to BGs and BGCs involves surface modifications. Another factor that could potentially affect drug release dynamic was modification of BGs surface. In relation to this, Farag and colleagues (Farag *et al.*, 2015) have examined the effect of gamma-irradiation (25 and 50 kGy) on the vancomycin release from nano-bioactive glass (labeled as G25 and G50). These examiners noticed that diffusion from the spherically shaped NBG carrier was the main mechanism of drug delivery.

Considering the future, the usage of BGs and BGCs in ophthalmology can disclose as well new therapeutic approaches for the treatment of ocular tumors. The magnetic features of the Fe-containing glass can be exploited for in situ cancer treatment by hyperthermia. Hyperthermia using implantable magnetic BGs and BGCs has emerged as a promising option for the localized treatment of malignant tumors (Vallet-Regi and Ruiz-Hernandez, 2011).

Conclusions

Bioceramics have a great potential in ophthalmic surgery due to a set of unique features that can be properly and successfully exploited for ocular applications. They have found their application in three types of ophthalmic surgery such as orbital implants for anophthalmic patients, oculoplastic surgery for orbital floor repair, and ocular keratoprosthesis (artificial cornea). So far, it is almost impossible to give the final answer which is the most fitting bioceramic material for the repair of orbital floor fractures, orbital implants or artificial cornea? Porous bioceramics stimulate fibrovascular in-growth, which is a fundamental feature to stabilize the implant in the defect, to secure an appropriate motility of ocular prosthesis and to reduce the risk of infection after the surgery to a minimum. Porous bioceramics have been also demonstrated to allow and even stimulate keratocytes adhesion and proliferation, which make them promising candidates for the development of a new and improved kind of keratoprosthesis skirts. It has been suggested recently that BGs and BGCs possess a unique power of stimulating tissue regeneration and cell activity in vivo. The extraordinary versatility of these biomaterials, which primarily depends on the flexibility of their structure, allows various applications in ophthalmology. Their chemical, mechanical and bioactive characteristics could be designed by varying the glass composition (type and amount of inorganic oxides) or applying appropriate processing routes. Considering the future, bioactive glasses and glass-ceramics can improve the performance of ocular implants imparting them key extra-functionalities such as antibacterial features via the release of adequate metal ions, controlled drug release, to elicit an angiogenic and anti-inflammatory effect at the implant site. Novel perspectives can raise from the use of mesoporous oxide-based materials for in situ drug release, magnetic and radioactive bioceramics for ocular tumor treatment.

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Biomaterials for Bone Tissue Engineering: Properties and Applications

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Introduction

Tissue and organ still pose a challenge in contemporary medical trial. There are other treatment options which include transplantation (xenotransplantation), mechanical devices, artificial prostheses, surgical repair and drug therapy. In spite of all the method mention, if the organ and tissue suffered significant damage, it can neither be repaired nor is long-term recovery going to help restore the normal biological function of the tissue. Tissue engineering (**Fig. 1**) is one of few emerging fields that focus solely on developing alternative treatment for tissue and organ repair. It is a multidisciplinary field that uses a combination of cells, engineering materials and suitable biochemical factors to enhance or replace biological function to produce a better clinical procedure to repair damaged tissues and organs [1–3].

In tissue engineering, a new tissue usually derived from patients (bone marrow or muscle biopsy) to avoid any immune response issues by using the patient's own cells is regenerated from the cells seeded onto a bioabsorbable scaffold, occasionally incorporating a few treatment methods to overcome clinical limitation which includes growth factors, nanomedicine and gene therapy. It is possible to create all sort of tissue theoretically based on basic principle of tissue engineering. Tissue engineering application often revolve around the usage of three-dimensional (3D) scaffold. In order for the tissue and organ to regenerate successfully, based on concept of engineering tissue; one of the critical elements to that should be considered includes the biomaterial scaffold (natural or biodegradable synthetic structure) that serve a mechanical support and provide a suitable microenvironment to support cell growth, progenitor cells that can be differentiated into specific cell types, and inductive growth factors that can modulate cellular activities [1,2,4,5].

Biomaterials are incredibly significant in tissue engineering in various ways such as; acting as a substrate so that cell populations can attach and migrate, as a cell delivery vehicle, 3-D implant with a combination of specific cell types, to activate specific cellular function in the localized region as a drug carrier, to define the shape of regenerating tissue as a mechanical structure, and to provide space as a barrier membrane for tissue regeneration along with prevention of fibroblast ingrowth into the space [4].

Hence with all the facts in mind, the aim of this paper is to do a thorough study and review on the specific research on the biomaterial's applications and properties for bone tissue engineering which hopefully could discover a more suitable and affordable biomaterial which can substitutes and represent the future of new therapeutic approaches specifically aimed at clinical applications.

Biomaterial for Bone Tissue Engineering: Criteria

Natural bone is made of inorganic fraction and organic fraction (1/3 of the mass, mostly collagen). The inorganic fraction consists of 2/3 of the dry matter and which mostly includes 85%–90% of calcium phosphate, 8%–10% of calcium carbonate, 1.5% of magnesium phosphate and 0.3% of calcium fluoride. The minerals are present as apatite crystals, mainly hydroxyapatite [6]. **Table 1** shows the physical properties of human bone tissue which can be used to serve as a reference for the scaffolding materials.

Therefore, the materials used for bone tissue engineering must fulfill several requirements before the development and construction of scaffold. These includes:

(1) *Biocompatibility.*

Biocompatibility of the scaffolding materials is the basic requirement for tissue engineering where cell must be functional, adhere and eventually migrate on the surface of the scaffolding materials and begin to undergo proliferation before forming a new matrix. The scaffold material must support appropriate regulation of cell behavior (adhesion, differentiation, migration, proliferation, biomineralization, etc.) without causing chronic infection and displays systemic cytotoxicity to ensure a new desired tissue is functional. After the implantation, scaffold must be capable of inducing negligible of immune reaction to prevent rejection from the body. If the biomaterials are biologically incompatible, it will cause inflammatory reaction, toxicity, teratogenicity, hemolysis, and coagulation reactions which jeopardize the safety and health of the human body [7–10].

(2) *Biodegradability*

Biodegradation is a physiological process. Since the scaffolding biomaterials are not intended to serve as a permanent construct, it should gradually degrade so that the cell is able to form their own extracellular matrix and induce the ingrowth of new cell to replace the implanted scaffold or tissue engineered construct while being able to excrete from the body naturally without any interference (cell phagocytosis, dissolution, enzymatic hydrolysis, etc.). Ideally, the rate of degradation of scaffold should correspond with the formation of new tissue so that the implantation site (scaffold) is fully replaced by the new desired tissue while undergoing smooth transition of load transfer from scaffold to the new tissue. Degradation of biomaterials of scaffolding should also be controllable to match with different growth rate of tissue since it varies from

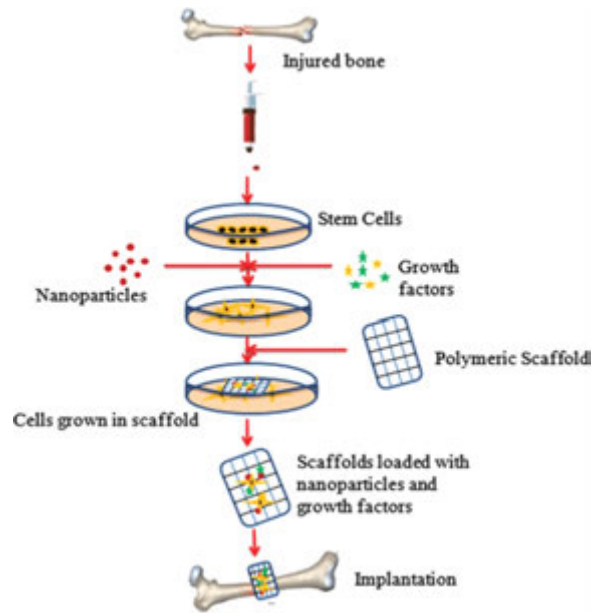


Fig. 1 Bone tissue engineering. Reproduced from Shukla, A., Dasgupta, N., Ranjan, S., Singh, S., Chidambaram, R., 2017. Nanotechnology towards prevention of anaemia and osteoporosis: From concept to market. *Biotechnology & Biotechnological Equipment* 31 (5), 863–879.

Table 1 Physical properties of human bone

Tissue	Tensile strength (MPa)	Compressive strength (MPa)	Young's modulus (GPa)	Density [g cm^{-3}]	Fracture toughness [$\text{MPa}^{1/2}$]	Elongation (%)
Cortical bone	164–240	100–230	7–30	1.8–2.1	3–6	1.07–2.10
Cancellous bone		2–12	0.01–3.0			0.5–3

different part of applications (craniomaxillofacial scaffolding require 3–6 months while spinal fusion scaffolding require 9 months or more than that) [9,10].

(3) *Osteoinduction and osteoconduction*

A good osteoinduction and osteoconduction bone scaffold will promote maximal growth factor in bone tissue along its surface or internal pores and it will also promote the proliferation of bone marrow mesenchymal stem cells (MMSCs) to differentiate into osteoblasts which will aid in the formation or mineralization of new external bone matrix [7,8].

(4) *Porosity, pore diameter and pore structure*

The ideal bone scaffold structure of interconnected porosity should be more than 90% together with a large specific surface area to promote and enable cell adhesion and growth, metabolite discharge, nutrient and oxygen entry, bone ingrowth into the material. This will ensure the desire shape and mechanical strength of the bone structure. The ideal pore diameter of the material of bone scaffold should mimic and be as close as possible to the actual size of the normal bone unit (the bone unit of an average human size is about 223 μm). In general, the acceptable size of a scaffold pore diameter is between 200 and 400 μm [7,8].

(5) *Mechanical performances*

The foundation of a success implant for tissue engineering lies on the properties of the material (elastic stiffness, toughness and strength). The scaffolding materials must have enough stiffness and mechanical strength for surgical handling during implantation and be consistent with the host tissue. The scaffolding implant must have the enough mechanical integrity to allow the formation of new tissue during implantation time until the end of the remodeling process. Excess stiffness in the bone scaffold will result in high stress shielding phenomena. In the end, it will ultimately result in the failure of the bone regeneration as the load cannot be transferred from the implant to the adjacent bone effectively, causing insufficient mechanical stimulation from filled autogenous bone and the original cancellous bone which results in the occurrence of bone tissue absorption and loosening of the implant. On the other hand, if the stiffness is too low, it will not meet the standard mechanical strength requirement for as the bone is not able to carry or withstand higher load of carrying capacity making the bone more prone to fracture. The biomaterial of bone should also have high plasticity so that can be machined easily and retain its shapes in the body longer [7,9,10].

Table 2 Mechanical properties of non-degradable metallic materials

Material	Tensile strength (MPa)	Compressive strength (MPa)	Young's modulus (GPa)	Elongation (%)	Density [g cm ⁻³]	Degradation and loss of mechanical strength
Stainless steel	460–1700	500–1000	180–205	10–40	7.9–8.1	None
Titanium alloy	900–1000	900	110–127	10–15		None

Biomaterial for Bone Tissue Engineering: Applications and Properties

Bone tissue scaffold material can be classified into two categories:

- (1) Biodegradable
- (2) Non-biodegradable.

Non-biodegradable scaffold materials were widely used in the past. These materials have common properties which are characterized by high mechanical strength, excellent resistance to fatigue, deformation and wear, and biological inertness (resistant to acid-base changes, anti-aging). However, non-biodegradable material causes medical complication such as secondary surgery problem. Thus, biodegradable material is more preferred at present. Most of the contemporary bone tissue scaffold materials are made of biodegradable and composite (combination of biodegradable and non-biodegradable) materials which are extensively used in research and treatment [7].

Metal material

One of the earliest biological material develop for human use were metal materials. These materials are extensively used to produce artificial joints, artificial prostheses, medical instruments and so on. Metal materials were commonly used as it exhibits a high mechanical strength and toughness, excellent resistance to fatigue, easy to shape and affordable which helps in regeneration of bone, teeth and other parts that bear high loads [7]. Accident like trauma, pathology and resorption often cause fracture in bone tissue. Titanium, stainless steel and its alloy are often used in most of the fracture fixation treatments since bone fixation and repair devices traditionally have been fabricated with metals and clinically practical [11]. Table 2 below shows the properties of non-degradable metallic biomaterials that are often used as an implant for bone.

The disadvantages of these metallic implants and devices required a second surgery to be removed from the body since it is not biodegradable. It can also cause stress shielding phenomena where the implant loosens as well as undesired bone resorption due to the mechanical forces and load being retained by the implants instead of transferring to the healing bone. The main causes of stress shielding are the mismatching of mechanical properties between the bone and these devices. Besides that, the corrosion process of metal materials induced by physiological environment due to the release of wear particle and metal ion to the surrounding tissues. The mechanical stress and electrochemical or cellular reactions cause the release of these particle and ion. It may not directly influence osteolysis and aseptic loosening, but they will become bioactive and destructive if react with bio-molecules which may lead to toxicity and unpleasant side effect. The young modulus of the implants play an important role as well because the higher the young modulus the most likely it will cause stress shielding which inhibit the existing cell from mechanical stimulation (the ability to transfer physiological stress to bone tissue) [6,7,11,12].

To resolve these problems, researchers explore extensively various method to improve the biocompatibility of the material. In recent year, most of scaffold metal material are made of composite material which includes stainless steel, cobalt-based alloy, and titanium-based alloy. A rabbit model is used to test a new biodegradable scaffold material based on magnesium alloy which results in the success of promoting higher rate of bone formation and suitable degradation. It not only further improved osteoblast activity but also decrease the number of osteoclasts temporarily due to the corrosion product of magnesium hydroxide [6,7,12].

Ceramic materials

Calcium phosphate (Cap) ceramics is also one of the most common scaffold materials for bone tissue. Due to its different chemical composition (Ca/P-ratio) and forms, it can be combined into different composition such as biphasic calcium phosphates (BCP) or remain as natural occurring mineral form such as hydroxyapatite (HAp), tricalcium phosphate (TCP) [12].

Calcium phosphate ceramics is used as a bone substitute extensively due to their physical properties (degradation rate, stability and processability) can be modified into a wide range of composition. The porosity of the ceramic scaffold must mimic as close as possible to the actual size cancellous bone (range from 300 to 500 µm) to cultivate the ideal environment for osseous ingrowth. A special manufacturing technique is required to ensure the presence of interconnected porosity in the ceramic material to prevent low oxygen tension due to blind which can prevent osteoblastic differentiation from taking place [12].

Calcium phosphate ceramics naturally has no osteogenic or osteoinductive properties. They are characterized by having an excellent biocompatibility and are bioactive as they attach to the bone and improve tissue formation. The combination of different type of ceramic (structure and Ca/P ratio) is similar with the mineral phase of a natural bone. Thus, it will naturally induce a mechanism to release calcium and phosphate ion to bind and form a connection between the ceramic and bone (bonding

Table 3 General properties of natural scaffold

<i>Properties</i>	<i>Natural scaffold</i>
Biocompatibility	Varies depending on the source of the biomaterials.
Biodegradability	Degradation rate are not defined.
Differentiation	Retain the local integrin binding sites.
Reproducibility	Highly maintained local architecture. Great variability between scaffolds donor.
Storage duration	Long term storage conditions show degradation.
Immunogenicity	Decellularization process remove antigen content.

osteogenesis) which will result in the accumulation of woven bone onto the ceramic surface without separating the layer of connective tissue and is converted to lamellar bone during the course [12].

Ceramics have two different depletion mechanisms:

- (1) Reabsorption: An active cellular process where consecutive neoformation of bone is induced by osteoclasts.
- (2) Degradation: A chemical process that takes place in a humid environment.

The absorption rate varies from different type of ceramic material and composition as well as the manufacturing technique. Tricalcium phosphate (TCP) are often used and combine with other composite material as it is reported to eliminate osseous ingrowth [12].

The main disadvantages of ceramic usage in clinical is due to its low brittleness and mechanical strength. It insufficient and cannot withstand high load as weight bearing component even with adequate porous design [12].

Polymer

Polymers are characterized by having a good processability, biocompatible, versatility in chemistry and degradable. Polymer that has high biodegradability ultimately can prevent problems related with stress shielding after recovery, act as a therapeutic drug delivery to fight against infection or to accelerate new bone growth by stimulating the growth factor in the body. They have shown to be a great potential to serve as scaffolding material as it has a wide range of relative molecular mass (tens of thousands to several million), which are often used for tissue engineering (bone, joint, cartilage and soft tissue) organ substitutions (liver, heart valve, bladder and pancreas) and various other tissue [7,13].

Polymer scaffold has a wide range of usage and can be made into biological or synthetic, degradable or non-degradable depending on the properties (composition, structure and constituent macromolecules) of the polymer. Polymers can be classified into two categories:

Natural polymer

For bone tissue engineering, most of the commonly used natural polymer is hyaluronic acid, collagen, silk, fibrin, chitosan and alginate. They can also be classified as proteins (collagen, myosin, fibrinogen, gelatin, keratin, elastin, actin, and silk), polysaccharides (cellulose, glycosaminoglycans, chitin, dextran, and amylose), or polynucleotides (DNA, RNA). Natural polymer is considered as one of the first biodegradable material used clinically for a long time. Natural polymer such as collagen has a good biocompatibility and does not cause any harmful effect (irritation, inflammation or toxicity) after implanting into the human body. Besides enhancing cell proliferation and increase the rate of wound healing, the degradation of the product does not cause any adverse side effect and toxicity to the host. Fibrin (mainly from plasma protein) on the other hand, has a good compatibility with blood and tissue. It does not cause any toxicity and typically used in filling bone defect after surgery [7,12,14]. Table 3 below shows the general properties of natural polymer which can be used as scaffolding.

Collagen

Collagen is a group of protein that has characteristic molecular structure (fibrillar) which contributes to the extracellular scaffolding. Collagen can be found most abundantly as structural protein in the body and serve as a primary component of extracellular matrix (ECM). Collagen has great potential to produce bone by culturing cells since one of the two major components of bone consist of collagen where it makes up of 89% of organic matrix and 32% of volumetric composition of bone. Collagen has properties that are low in elasticity and poor mechanical strength but relatively stable (bonded by covalent cross-link formation). They are biodegradable, biocompatible and non-cytotoxic which can be considered as an alternative for synthetic materials in biomedical applications due to its low inflammation, antigenicity biocompatibility and cytotoxic responses [15,16].

Hydrogels

Hydrogels have viscoelastic material properties that is suitable for cartilage regeneration. It provides a high level of water content in 3-D cellular microenvironment due to its gelling system and minimal invasive manner. Hydrogels have a relatively straightforward cell encapsulation, delivery and chemical biofunctionalization. Hydrogels that is made up of naturally derived macromolecules

Table 4 Natural and synthetic polymer-based hydrogels for bone tissue applications

<i>Natural polymer</i>	<i>Synthetic polymer</i>
Alginate	Polyethylene glycol (PEG)–polylactide (PLA)
Peptide amphiphile–Ti composite	Polyethylene glycol (PEG)
Chitin	
Hyaluronic acid (HA)	

potentially have many advantages in term of degradability of cell-controlled, biocompatibility and intrinsic cellular interaction. They can be made from either natural or synthetic polymers that are either cross-linked through covalent or non-covalent bonds. Covalent cross-linked network will result in gels form. Hydrogels are biocompatible with human body since it is structurally similar with macromolecular based components that can be found in the body. Hydrogels that is made from natural polymer generally has limited range of mechanical properties and exhibit variations in batch in comparison with synthetic polymer where it can be prepared with precise controlled functions and structure. To fulfill the tissue engineering design criteria, all biodegradable hydrogels must have a well-defined degradation behavior, adjustable through hydrogel structure or chemistry and reproducible. Currently, hydrogels that are biocompatible are being used as drug delivery carriers, bone healing and cartilage wound healing. They have properties that are favourable to promote angiogenesis, cell migration, rapid nutrient diffusion and high-water content. The combination of hydrogels and growth factor enable the development and differentiation of cells in newly formed tissues. Intensive studies are carried out on hydrogel scaffold for tissue engineering to serve as a replacement for connective tissue due to its biochemical which is similar to the highly hydrated glycosaminoglycan (GAG) component of connective tissues [14,17]. **Table 4** shows the hydrogel-forming polymers for bone tissue engineering.

Chitosan (CTS)

Chitosan is a linear polysaccharide made of N-acetylglucosamine and glucosamine that is bounded together by β -(1,4)-glycosidic bonds. Chitosan is a bioactive copolymer which is defined by two major properties, including molecular weight and degree of acetylation (DA). Chitosan is widely used in biomaterials in bone tissue engineering due to its natural properties like high biodegradable, biocompatible, osteoconductive, osteoinductive, porous structure, low toxicity, suitable for cell proliferation and has been proven countless studies to be capable of combining antibiotic with chitosan-based dressing. Chitosan is capable of interacting with negatively charge polymers and structural molecules that exist in extracellular matrix (ECM) due to chitosan being the only biopolymer that is positively charged. Chitosan has wide range of application such as acting as a drug carrier and coating molecule to helps to make chemical modification, aids in wound healing, utilised as a drug delivery and cartilage tissue engineering. In term of bone regeneration application, chitosan can be made into several different forms which includes hydrogels, particle, films, foams fibers and sponges and have several methods of processing ranging from physical blends (where polyelectrolyte complexes is formed) to novel approach like rapid prototyping and electrospinning [13,16,18].

Synthetic polymer

Synthetic polymer exhibits controllable properties (degradation time, porosity and mechanical characteristics) which can be modified to suit specific function and application. The most commonly used synthetic polymer in tissue engineering is Polylactic acid (PLA), Polyglycolide (PGA) and poly (lactic-co-glycolic acid) (PLGA). Synthetic polymer such as polylactic acid is bioactive and has a material bending strength of more than 120 MPa due to its properties which inhibit tissue stimulation. It is suitable to be bone scaffold material because it will eventually be metabolized and completely absorb by the body without any harmful effect. This makes implantation of scaffold much more convenient and less risky without having the material to be removed later [7,12,14]. **Table 5** shows the general properties of synthetic polymer which can be used as scaffolding.

Polyesters

Biodegradable synthetic aliphatic polyesters are most commonly used as synthetic polymer for bone tissue scaffold material. There are made of saturated poly- α -hydroxy esters which includes poly (lactic-co-glycolic acid) (PLGA), polylactic acid (PLA) and polyglycolide (PGA). The polymer in this family besides PGA can be processed by using a variety thermal and solvent based method because of they are soluble in most of the common organic solvent. This includes fibre meshing, porogen leaching, supercritical fluid processing, microsphere sintering, 3-D printing, phase separation and gas foaming to produce different type of porosities and surface characteristic of 3-D scaffolds. The major drawback of polyesters is the inflammation reaction caused by its degradation which reduces the local pH value and may accelerate the polyester degradation rate [16,17,19].

PLA exist in three forms:

- (1) Poly-D-lactide (PDLA).
- (2) Poly-L-lactide (PLLA).
- (3) Poly-DL-lactide (PDLLA).

Table 5 General properties of synthetic scaffold

<i>Properties</i>	<i>Synthetic scaffold</i>
Biocompatibility	Biocompatibility is very poor.
Biodegradability	Poor biodegradability. The by-products have potential to cause toxic during degradation.
Differentiation	Absence of specific integrin binding site it relies on engineered scaffold.
Reproducibility	The architecture is very complex. Can possibly be controlled.
Storage duration	Improved storage stability and durable.
Immunogenicity	Highly depend on the type of material as the contents varies and unknown.

PDLLA

PDLLA has a very good features with respect to implant performance, it shows an excellent biocompatibility in vivo and high mechanical stability with good osteoconductive potential. PDLLA is can be used as a biomedical orthopaedic coating material and due to its low molecular weight, PDLLA can act as local drug delivery system by combining with drugs like antibiotics, growth factors or thrombin inhibitor [19].

PCL

PCL belong to aliphatic polyester family and can be considered as drug-delivery system that can be used entrap antibiotic drugs. This polymer has various properties have been studied extensively as biomaterial such as low melting point (59–64°C), high thermal stability, biocompatibility, and biodegradability. PCL is also used to enhance the treatment of bone defects by improving bone ingrowth and regeneration. PCL and its copolymers have the same degradation mechanisms as PLA which involve 2 stages: diffusion (weight loss) of oligomeric species from bulk and random hydrolytic ester cleavage. High molecular weight (50,000) has a slow degradation rate and require 3 years to remove from the host body. Combination of PCL and HA increases the composite compression modulus, however the changes in the composite mechanism between plastic to brittle (easy to rupture) lowered the mechanical properties of PCL and other biodegradable polymers [16,19].

PPF

PPF is an unsaturated linear polyester that can be cross-linked by double bond reaction using photochemical or thermal radical polymerization. The upside of this polymer is the degradation products produced (propylene glycol and fumaric acid) are biocompatible and can be eliminated from the body easily. The polymer double bond allows cross-linking in situ, which causes hardening in the moldable composite within 10–15 min. The mechanical properties of PPF can be control by regulating cross-linking conditions, suitable molecular weight control and incorporation of reinforcement. There is suggestion where PPF is used as a scaffolding material to guide tissue regeneration where it serves as a part of injectable bone replacement composite [19]. Table 6 shows the properties of bioabsorbable polymeric scaffold materials.

Nanomaterials

Carbon nanotube (CNT)

Carbon nanotubes (CNTs) are structures made of graphitic tubular. It has been recorded that the length-to-diameter ratio of nanotubes is roughly up to 28,000,000:1. Carbon nanotubes are mostly used in many applications which includes optic, material sciences, nanotechnology and electronics. CNTs are introduced as biomaterials for bone scaffold is due to its remarkable mechanical properties (Table 7), chemical and electrical properties. They are mainly used in prostheses for delivering drug into the system, fixing fracture and bone scaffolding for tissue regeneration. It has been shown that in vivo or composites, CNTs is able to enhance the biocompatibility and mechanical properties of composite biomaterial due to its capability of interacting with cell binding protein, changing cell shape accordingly to cell-binding affinity, regulating stem cell differentiation and is able to accelerate bone formation with the help of human bone morphogenetic protein-2. CNTs can be used to develop controlled nanoscale texture and patterns over substrates. CNTs have high conductivity which is used to study the proliferation effect of electrical activity and stimulation on cells. It is made of rod like shape and nanoscale dimension that allow them to act like morphological biomimetic of the fibrillar proteins in the extracellular matrix (ECM) [13,20].

CNTs can be divided into two categories:

- (1) Single-walled carbon nanotubes (SWNTs).
- (2) Multi-walled carbon nanotubes (MWNTs).

Single-walled carbon nanotubes (SWNTs) are made of single layer tubular graphitic carbon while multi-walled carbon nanotubes (MWNTs) are made of multiple layer of tubular graphitic carbon (between 2 and 40) [13,20].

Table 6 Mechanical properties, biocompatibility and biodegradation of polymeric scaffold materials

Polymer	Melting point T_m (°C)	Glass transition point (°C)	Biodegradation time (months)	Compressive or tensile strength (MPa)	Modulus (GPa)
Poly (D, L-lactide)	Amorphous	55–60	12–16	Pellet: 35–150	Film or disk: 1.9–2.4
Poly-L-lactic acid	173–178	60–65	>24	Film or disk: 29–35 Pellet: 40–120	Film or disk: 1.2–3.0 Fibre: 10–16
Poly (Glycolic acid)	225–230	35–40	6–12	Fibre: 870–2300	Fibre: 7–14
Poly (lactic-co-glycolic acid)	Amorphous	45–55	Adjustable: 1–12	Fibre: 340–920	1.4–2.8
Poly (Propylene Fumarate)			Bulk	41.4–55.2	
Polycaprolactone	58	–72	>24	2–30	
Poly (D, L-lactic-co-glycolic acid) (50/50)	Amorphous	50–55	3–6		1.4–2.8
Poly (D, L-lactic-co-glycolic acid) (85/15)	Amorphous	50–55	3–6		1.4–2.8
Poly (D, L-lactic-co-glycolic acid) (90/10)	Amorphous	50–55	<3		
PHA and blends	120–177	–2 to 4	Bulk	20–43	
Polyanhydrides	150–200		Surface	25–27 30–40	0.14–1.4
Polyorthoester	30–100		Surface	4–16	2.5–4.4
Polyphosphazene	–66 to 50	242	Surface		
Polydioxanone	NA	(–10) – 0	>2		1.5

Note: Rezwan, K., Chen, Q., Blaker, J., Boccaccini, A.R., 2006. Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering. *Biomaterials* 27 (18), 3413–3431.

CNTs is capable of interacting with collagen fibers at a molecular level and relax its helical structure. There are several authors that has developed composites and scaffolding material with CNT, it can be observed that multi-walled carbon nanotubes (MWNTs) coated dish have a higher cell adhesion compare to collagen coated dish. Addition of CNT in the composite help to increase the stiffness of scaffold greatly due to its rigidity. CNT also improves the performance or functionality of collagen as it effectively increases the neural differentiation of stem cells [13,20].

Composite

Chitosan (natural polymer) + hydroxyapatite (HAp) (ceramic)

Hydroxyapatite (HAp) and chitosan serve as one of the best bioactive biomaterials since both materials have an exceptionally high biocompatible with human body. Chitosan scaffold itself cannot mimic all the properties of natural bone because by nature chitosan are flexible and mechanically inferior to normal human bone. Chitosan is not osteoconductive as it does not load bearing bone implant. However, with the addition of ceramic (hydroxyapatite) materials, it greatly improves the mechanical strength and osteoconductive properties of chitosan. The development of composite biomaterial (chitosan and hydroxyapatite) can imitates all the properties and the function of an actual bone. The natural polymer in the composite material can mimic the organic portion of the natural bones and improved the mechanical properties (Young's modulus, fracture toughness, compressive strength) of hydroxyapatite, while the osteoconductive ceramic is able to imitates the inorganic portion as well. Based on Table 8, the maximum compressive strength that can be achieved by different composite ratio of chitosan/HAp is 119.86 MPa. Composite (chitosan combines with HAp matrix) produced using by blending methods results in weaker mechanical bond which is 47.8 MPa due to the decrease in interfacial bonding [13].

Factor that effect the properties of chitosan/HAp composite:

- (1) Ratio of Hap: Higher ratio of HAp has higher compressive strength.
- (2) Molecular weight scaffold: High molecular weight chitosan scaffold has higher the compression modulus compared to medium molecular weight chitosan.
- (3) Temperature: The higher the temperature, the stronger the interfacial bonding which increases the mechanical properties of the composite material.
- (4) Water content: The mechanical strength may depend on the amount of water content in a scaffold based on Table 2.

Poly(lactide-co-glycolide) PLGA + hydroxyapatite (HA)

To improve further the compressive yield strength of polymer, poly(lactide-co-glycolide) (PLGA) created by solvent particulate or casting leaching was crushed and then compressed along with hydroxyapatite (HA) [8].

Table 7 Mechanical properties of carbon nano tubes (CNTs)

Material	Young's modulus (TPa)	Tensile strength (GPa)	Elongation (%)	Aspect ratio	Size
Carbon nanotubes	1.0–1.8	30–200	10–30	>1000	1–10 nm in diameter

Table 8 Mechanical properties of chitosan/HAp composite

Compressive strength	Composite ratio	Method/state
119.86 MPa	30:70 chitosan/HAp	Blending methods
47.8 MPa		Dry state
40 MPa	40%/30%/30% weight/volume HAp/CTS/carboxymethyl	Wet state
12 MPa		

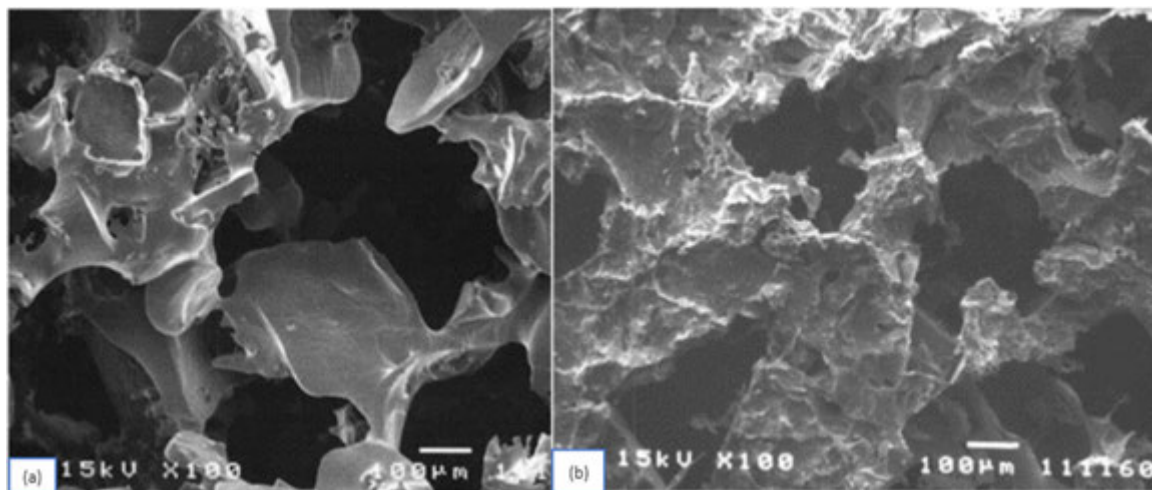


Fig. 2 (a) Electron micrograph of poly (propylene fumarate) PPF scaffold with 90 wt% of porogen and 10 wt% of poly (propylene fumarate) PPF. (b) Electron micrograph of poly (propylene fumarate) PPF scaffold with 70 wt% of porogen and 30 wt% of poly (propylene fumarate) PPF. Reproduced from Burg, K.J., Porter, S., Kellam, J.F., 2000. Biomaterial developments for bone tissue engineering. *Biomaterials* 21 (23), 2347–2359.

Poly (propylene fumarate) PPF + leachable component

The material that undergo polymerization can be altered (released of carbon dioxide) to cause foaming to produce a porous scaffold. It can fill irregular osseous defects due to the nature of the material (injectable) along with leachable component to enable more room for bone ingrowth as shown in **Fig. 2**. Both porogen in **Fig. 2(a)** and **(b)** are removed with water leaching after Poly (propylene fumarate) cross-linked [8].

Discussion

Generally, metallic biomaterials usually being used as a permanent implant to replace the defective bones or to serve as temporary framework (scaffold) as fixation device to stabilize bone and aids in regeneration of lost tissue function. Most of the metallic biomaterials has an excellent mechanical strength (tensile strength, compressive strength, yield strength and young modulus). Biodegradable metallic like Iron (Fe), Magnesium (Mg) and Zinc (Zn) are widely research currently for bone fracture fixation application. This is because biodegradable material like Fe, Mg and Zn degrades with human metabolism naturally and release necessary ions to aid in new bone tissue formation. Mg especially which found naturally in vivo is extremely biocompatible with bone tissue and plays an important role in metabolic function. Biodegradable metallic has better mechanical strength in comparison with biodegradable polymer to support bone healing process. Generally, biodegradable polymer is brittle and has a higher risk to cause tissue inflammation and necrosis. The duration and lifespan of the Fe, Mg and Zn scaffold can be controlled and are highly dependent on the type of alloying material as well as the method of processing. **Table 9** shows the rate of degradation and tensile strength biodegradable metallic in vitro for pure Fe, Zn and Mg.

Table 9 Rate of degradation and tensile strength of metallic biomaterials

<i>Metallic biomaterials</i>	<i>Degradation rate (mm year⁻¹)</i>	<i>Tensile strength (MPa)</i>
Fe (annealed)	0.16	200
Zn (cast)	0.2	20
Mg (cast)	407	86

Table 10 Advantages and disadvantages between different type of biomaterials

	<i>Advantages</i>	<i>Disadvantages</i>
Polymer	• Degradation attributes can be controlled by changing the constitution of individual polymer. • Physical properties that can be modified and can be mass produced. • Excellent biodegradability and biocompatibility over most metals and ceramics.	• Poor mechanical properties to withstand loading while undergoing degradation. • Limited amount of suitable natural polymer (chitosan, collagen and keratin) to serve as an implant material. • Unpredictable degradation mechanism (bulk-eroding polymers degrades over all cross section and have nonlinear erosion kinetics with discontinuities).
Metal	• Alloy's elements (Mg, Fe, Zn) are readily absorb by the body without harmful side effect. • Bioabsorbable materials has good in vivo biocompatibility to support bone regeneration. • Mg-based alloys able act like "smart" implants mainly due to its ability to stimulate cellular responses (increased in bone mass and mineral apposition) at molecular level in animal experiment.	• Metal ion released by biodegradable metal may accumulates in the tissue can cause potential health risk (cytotoxic, genotoxic and immunological effects) which causes reduction in biocompatibility. • Mg-based implant has no means to control (lack of metallurgical technology) the fast degradability and high corrosion rate before fracture heals. • Zn-based alloy has low plasticity and low strength which is not suitable to use as biomaterials for implants.
Ceramic	• Si and Ca ion released by bioglass enhance osteoblastic growth and differentiation. • Bioceramics have high compressive strength, good osteoconduction and bone integration as well as excellent angiogenesis. • Bioceramics is capable of triggering specific biological response by acting as a local delivery vehicle for active ions in recent study.	• Difficulty in forming desire shape and it is too brittle. • Bioceramic has very slow biodegradation rate (crystalline HA). • Silicate bioceramics can induce a series of immune response from host to cause chronic inflammation, formation of foreign body giant cells and tissue fibrosis which is damaging and harmful to the implant function (failure in regenerating the tissue).

However, there are some complication arise when contemporary metallic implants produce by inert material to replace permanently the bone tissue in the bone which includes stress shielding over-time, metal ions build-up in tissues and physical irritation due to chronic inflammation. Repeat surgery is needed for implants in growing bones due to the incapability of implants to adapt to the growth [21–26].

There is a lot of research done on polymer which includes natural and synthetic due to overcome some of the limitation of metallic biomaterial. Generally, polymer that has high biodegradability ultimately can prevent problems related with stress shielding after recovery, act as a therapeutic drug delivery to fight against infection or to accelerate new bone growth by stimulating the growth factor in the body. Polymers are biocompatible in bone tissue engineering with minimal adverse effect on immunological. Polymers have adjustable biodegradation rate, unstable (hydrolytically) and degradable (enzymatically) linkage in back bone which is used as delivering controlled bioactive molecules in bone tissue scaffold. Natural polymers have a higher biocompatibility compared to synthetic polymers, but it has lower mechanical properties and processability than synthetic. However, biological properties and physicochemical of synthetic polymers are predictable and can easily reproduced to achieve desired properties since it is synthesized under a more controlled condition.

Ceramics as standalone material has poor mechanical strength (brittleness) but it has good biodegradability and bioactive molecules that is capable of releasing potency at a controlled rate. Most of the studies often combine polymers with ceramics where the natural polymer in the composite material can mimic the organic portion of the natural bones and improved the mechanical properties (Young's modulus, fracture toughness, compressive strength), while the osteoconductive ceramic is able to imitates the inorganic portion as well [13,27–29]. Table 10 shows the comparison (advantages and disadvantages) between polymer, metallic and ceramic biomaterials for bone tissue engineering.

Emerging Trend

Recently a new class of metallic materials has been studied due to its potential use as biomaterials application. Bulk metallic glasses (BMGs) are considered as a new class for metallic materials. BMGs have a good combination of properties and possessed

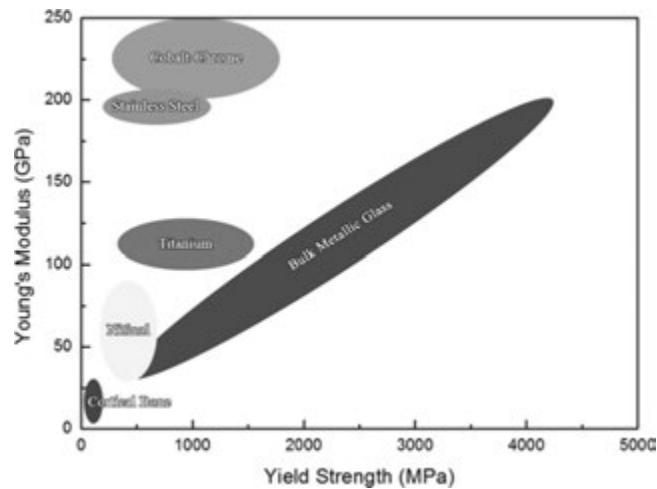


Fig. 3 Comparison of properties between metallic biomaterials. Reproduced from Meagher, P., O'cearbhail, E.D., Byrne, J.H., Browne, D.J., 2016. Bulk Metallic Glasses for Implantable Medical Devices and Surgical Tools. *Advanced Materials* 28 (27), 5755–5762.

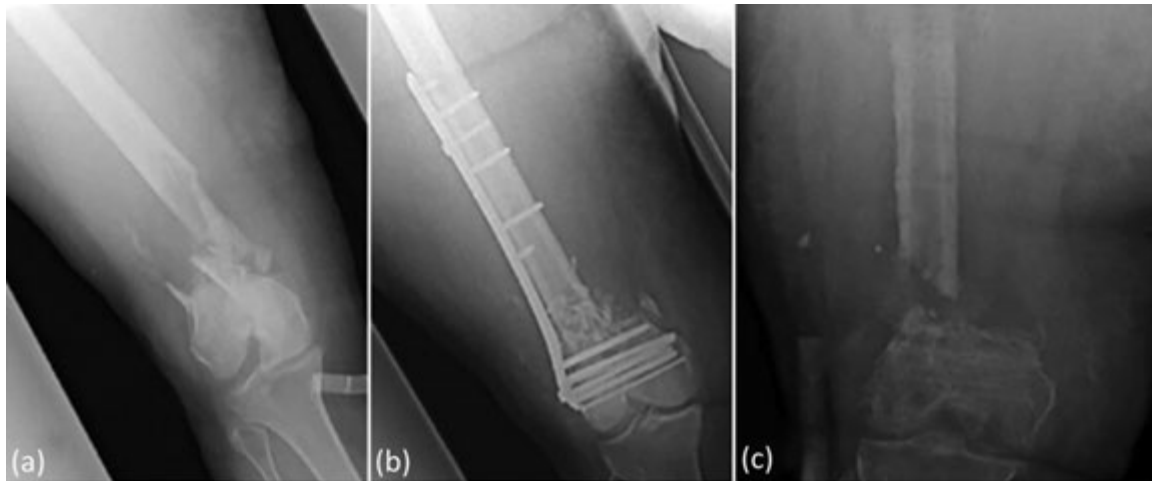


Fig. 4 Distal femoral fractures on right leg. (a) Radiographs image at bilateral femoral fracture, (b) Initial condition stabilize. (shortening and comminution of the right distal femur indicate post-traumatic infection therapy) (c) radiography image taken after removing plate and external stabilization of the right femur. (atrophic non-union). Reproduced from Winkler, T., Sass, F.A., Duda, G.N., Schmidt-Bleek, K., 2018. A review of biomaterials in bone defect healing, remaining shortcomings and future opportunities for bone tissue engineering. *Bone & Joint Research* 7 (3), 232–243.

capability to be applied in various type of implant application like bones. It is shown in vivo BMGs induced foreign body response while in vitro promote cell proliferation and adhesion. BMGs appeared atomically frozen liquid as it does not have long-range atomic order compared with conventional alloy that has crystalline structure. There are no dislocation and slip planes in BMGs due to its amorphous structure properties which results in excellent elasticity and strength. Its corrosion rate is significantly reduced compared to crystalline metals due to the absence of grain boundaries and their isotropic and homogenous nature or precipitates as oxidation sites. BMGs alloy have low cooling rate which can avoid crystallization during solidification.

In comparison with regular alloy, BMGs alloy have superior mechanical properties which include high tensile strength, high elastic strain limit and relative low modulus elasticity. **Fig. 3** shown below demonstrate the comparison of properties between metallic biomaterials (cobalt chrome, stainless steel, titanium nickel titanium) and cortical bone. Bioinert BMGs better corrosion and wear resistant than conventional alloys. It also has desirable corrosion rate, the strength decay inversely proportional to wound healing which restricts stress shielding phenomena and the ion produced from this process is non-lethal to where surgery is not needed to remove the device as it is completely absorbed inside the body.

However, the current challenges of BMGs lack of plasticity characteristic, lack of research and understanding about fatigue, stress corrosion and wear debris behavior and crack propagation which ultimately results in brittle failure. There is also a challenge in matching specific group on faculty affair (GFA) with the clinical needs and biocompatibility [21,22,30].



Fig. 5 Radiography image where both knees replaced with distal femoral replacements after resecting all infected and dead bone. Reproduced from Winkler, T., Sass, F.A., Duda, G.N., Schmidt-Bleek, K., 2018. A review of biomaterials in bone defect healing, remaining shortcomings and future opportunities for bone tissue engineering. *Bone & Joint Research* 7 (3), 232–243.

There is a focus in research on mechanical cues and signals in specific cellular behavior and differentiation whereby the manufacturing and design of scaffolds have expected, and optimal tissue development based upon the activation of mechanical stimulation and fluid perfusion. There is also method that increases the control of cellular differentiation such as scaffolds owning shape memory and conductive materials. Even though the development of biomimicking scaffolds could replace damaged bone, most of the bone scaffolds may not induce enough blood vessels and nerves. It causes the developed bone tissue and native bone tissue scaffolds to develop a gap in between them due to integration and regulation of multiple tissue types of the micro-environment of bone tissues. Scaffolding with neurovascularised networks are more accurate in mimicking the native skeletal tissues and is suitable to regenerate bone tissues [28].

In order to mimic the natural bone hierarchical structure which can be controlled by the substrate of the geometry, mechanical properties, biochemical properties and surface modification, there are various approaches that have been done which includes creating different type of biomaterials for different animal models. To understand the animal physiology, the overall system works as co-relation instead of being in an independent manner. Fundamental interconnections in bone tissue promote bone growth and remodeling. The blood vessel promotes neurogenesis (through oxygen, neurogenic growth factors and nutrient) and nerve fibers further improve the vascularization (through vasculogenic neuropeptides). The brain derived neurotrophic factor (BDNF) may promote osteogenesis indirectly through neurogenesis since it helps promote human bone mesenchymal cells (hBMSCs) osteogenesis and neurogenesis. Thus, the design for clinical applications is based on engineered neurovascularised bone scaffolds through biomimetic approaches [28].

At the same time, there is also a great interest in the development of bio-polyesters by using renewable resources due to the increase in petrochemical price, greenhouse emission and shortage of fossil fuel reserves. The advances of blends and composites of polyesters and hydrophilic natural have received significant attention as the development of novel biodegradable polyesters could lead to a suitable property for exceptional biomedical applications [16].

Difficulty and Challenges

One of the few current clinical difficulty and challenges faces for bone tissue engineering are the reconstruction of bone fractured. This is due to restricted amount of bone stock which affect the quality of bone, which obstruct the conventional method used to fix the rigid fracture. The defect that are most commonly encounter are from allogeneic or autologous bone which subsequently may lead to joint arthroplasty. Bone morphogenetic protein (BMP) infused into biomaterials to stimulate growth factor to actively induce new bone formation in cases of nonunion fracture has been withdrawn (BMP7) from the market due to several safety reason like pathogen transfection, and high risk of failure rate [31,32].

Another example of clinical challenges and can't be solved is the bone healing defect as shown in Fig. 4 where it shows the time course of patient receiving treatment after suffering from distal femoral fractures after falling from a certain height. Based on Figs. 4 and 5 demonstrate the various possible cause which prevent the bone from healing:

- (1) The injury from the fall cause the initial bone loss.
- (2) Local immune competence along with impairment of vascularization due to multiple surgical revisions.
- (3) Further bone loss cause by osteitis and osteomyelitis infection.

Different approach (current clinical standard) is taken to counteract the problem such as infection therapy (antibiotic), local therapy (BMP) and bone transplantation along with fixing internal and external procedures. However, all the approach fails to fight against infection and regenerate the bone which causes the distal femurs to resection. In the end, bilateral arthroplasty and implant for cortisol structure had to be carried out on both legs. It is still a challenge for the biomaterial for bone tissue scaffold to mimic the actual in vitro situation to get the same and desirable results [15,32].

The challenges in bone tissue engineering is to improve the mechanical strength of scaffolding materials. Material like carbon nanotube (CNT) can mimic the functionality of natural bone and serve as a promising biomaterial since it has strong mechanical properties. The uniform dispersion of composite material like CNT in chitosan (CTS) and HAP matrix posed a challenge since CNTs are in polymer matrix form and cannot be dispersed easily. It is also challenging to produce CNTs in pure form for biomedical applications because CNTs which contains metal are toxic to cells. The toxicity induces by CNT greatly rely on the type of cell, purity and functionalisation of CNT. Despite the progress made in making CNTs a controllable nanoscale, there little studied regarding the interaction between the effect of nanoscale on the cellular behavior. Synthetic polymers are widely used in composite materials for artificial bone besides chitosan (CTS), CNTs and HAP since the organic portion is important in bone implant. Thus, the composition of the scaffold matrices is often hybrid. Synthetic polymers show better results in cell proliferation, mineralization assays, alkaline phosphate activity, and cell viability. However, the major downside of synthetic polymer the degradation times which is half of natural polymer [13,20].

Conclusion

There is a change in approach over the years where metallic or synthetic implants and tissue grafting are replace by tissue engineering. A wide range of biomaterials often yield scaffold with different properties and applications. Biomaterials for bone tissue engineering plays a significant role by acting as artificial scaffold, matrices or construct. There are three distinct group of biomaterials that are most commonly used as scaffolding for bone tissue engineering, which includes, metallic, polymer (natural and synthetic) and ceramics.

Bulk metallic glasses (BMGs) are considered as a new class for metallic materials. BMGs have a good combination of properties and possessed capability to be applied in varies type of implant application like bones. In comparison with regular alloy, BMGs alloy have superior mechanical properties which include high tensile strength, high elastic strain limit and relative low modulus elasticity. However, the current challenges of BMGs lack of plasticity characteristic, lack of research and understanding about fatigue, stress corrosion and wear debris behavior and crack propagation which ultimately results in brittle failure.

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The challenges in bone tissue engineering is to improve the mechanical strength of scaffolding materials. Material like carbon nanotube (CNT) can mimic the functionality of natural bone and serve as a promising biomaterial since it has strong mechanical properties.

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Ceramic Matrix Composites in Total Hip Arthroplasty

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Glossary

Bearing surface The area of contact between two objects – femoral head and acetabular cap.

Ceramic material Hard, brittle, heat-resistant and corrosion-resistant material made from non-metallic minerals.

Ceramic matrix composite A group of composite materials consisting of ceramic fibers embedded in a ceramic matrix.

Composite material Material produced by combining two materials with different physical and chemical properties in order to obtain a superior material.

Introduction

Average human age is constantly rising. During the past three decades, life expectancy has increased from 64.2 years (1990) to 72.6 years (2019). This value is expected to increase to 77.1 years in 2050. The aging of the human population will have a huge impact on the society as it leads to a number of different health issues. Osteoarthritis is a progressive loss of joint cartilage which results with lower quality of life and it is one of the major causes for hip replacement procedure. One of the key factors for osteoarthritis in the human joints (knee, hip, spine and hand joints) is aging (Pivec *et al.*, 2012).

The hip joint belongs to a synovial joint which are the most flexible of the three types of joints that can be found in the human body. In the case of the synovial joint, the connection between the adjacent bones is not direct, instead they are in contact inside a joint cavity filled with a lubricating fluid. Beside synovial, there are also a cartilaginous (hyaline cartilage or fibrocartilage is responsible for connection between the bones) and a fibrous (fibrous connective tissue is responsible for uniting the bones) joint (OpenStax College, 2013).

The hip joint is one of two ball-and-socket joints (a subgroup of the synovial joints) of the body. The connection between the bones is established between the head of one bone, which is the ball part of the joint and the concave (the socket) part of the other bone. The main roles of this joint are to:

- (1) Provide stability to the human body during daily activities and
- (2) Support the body through the activities.

The ball part of this joint is the head of the femoral bone that is located at the proximal end of the bone, while the socket part is the acetabulum of the hip bone (Fig. 1).

Beside the femoral and the hip bone, this joint also has several ligaments that provide the joint stability by holding the femoral head inside the socket and the limitation of the leg's motion range in the hip joint (OpenStax College, 2013). These ligaments are (Hall, 2011):

- (1) Ischiofemoral ligament,
- (2) Iliofemoral ligament and
- (3) Pubofemoral ligament.

Total Hip Replacement (THR) surgery or Total Hip Arthroplasty (THA) is a surgery in which damaged parts of the hip joint are replaced with appropriate artificial ones (Derar and Shahinpoor, 2015). The hip joint needs to be replaced if it was damaged by an illness (e.g., arthritis) or if there are complex fractures which are not able to heal. Often, THR is the only option to restore patient's mobility. This is considered to be one of the most successful procedures in the world. Annually, more than 1 million hip replacement surgeries are performed worldwide, while it is anticipated that this number will double in the next decade (Shan *et al.*, 2014).

Major factors that influence the success of an implant are (Park and Lakes, 2007):

- (1) The properties and biocompatibility of the implant,
- (2) The health condition of the recipient and
- (3) The competency of the surgeon who implants and monitors its progress.

There are two types of hip replacement procedures:

- (1) Partial hip replacement and
- (2) Total hip replacement.

Artificial hip joint consists of femoral ball, femoral stem and acetabular cup. Total hip replacement is a technique where both the damaged bones (femoral bone and acetabulum) and the cartilage are removed and replaced with prosthetic components, while the partial hip replacement includes only the replacement of the femoral head of the damaged hip joint.

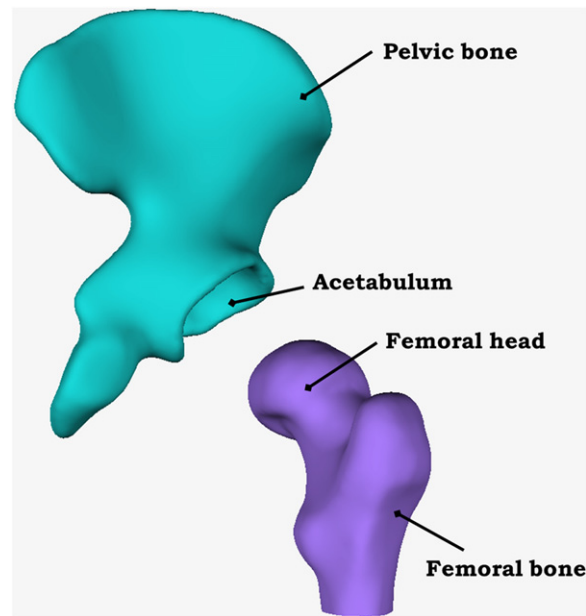


Fig. 1 Hip joint.

THR consists of the following steps:

Step 1. A surgeon makes an incision cut over the hip joint that needs to be replaced.

Step 2. In order to insert femoral part of the hip implant (femoral stem and ball), a surgeon must remove the damaged femoral head.

Step 3. If the complete joint is being replaced (THR), this step includes the removal of the worn out cartilage in order to make place for acetabular cup.

Step 4. An artificial socket is placed and fixed into place.

Step 5. In this step, the femoral bone is prepared for the stem placement. This includes cleaning and enlarging the hollow center of the femur in order to insert the femoral stem. A ball is attached to the upper part of the femoral stem.

Step 6. A spacer is placed between the socket and ball in order to provide smooth gliding for the artificial joint.

Depending on the fixation of femoral stem, we distinguish between two types (Morshed *et al.*, 2007):

- (1) Cemented and
- (2) Uncemented fixation.

Cemented fixation requires an additional layer between the bone and the implant to quickly establish the attachment between the bone and the implant. For this layer, usually the acrylic cement is used. In the case of uncemented fixation, implant surfaces are semi-porous, as it allows the bone to grow into the implant and form the attachment.

Considering the amount of THRs that have been performed, it is important to think about ways to improve artificial hip implants. Constant improvements in technology are necessary in order to make advances in this field. Based on the current limitations of the available hip implants, future research in this field will be oriented toward things: development of prosthesis with material properties similar to the bone material properties (Wirtz *et al.*, 2000; Gao *et al.*, 2019); improvement of implant design in order to obtain better and longer bone-implant connection (Vulović and Filipović, 2019; Apostu *et al.*, 2018); development of materials with improved wear characteristic (Khanna *et al.*, 2017; Merola and Affatato, 2019) and patient specific prostheses designed to improve prosthesis fit and increase implant's longevity.

Biomaterials Used for Hip Implants

Numerous biomaterials have been used in the field of orthopedic and they are being developed as engineers have not yet been able to develop the ideal biomaterial. Biomaterials used in this field need to comply with several requirements. The requirements are good biocompatibility, nontoxicity, good corrosion resistance, durability, high strength and ductility and low Young's module of elasticity (Adamovic *et al.*, 2018).

In total hip replacement surgery, both the acetabular and femoral bearing surfaces have to be replaced. Materials used for these surfaces have changed a lot during the past century. Usually, these parts of the hip joint are replaced with one of the following material combinations (Merola and Affatato, 2019): metal-on-polyethylene (MoP), ceramic-on-polyethylene (CoP), ceramic-on-ceramic (CoC) and metal-on-metal (MoM). The ideal bearing surface should have the following features (Minakawa *et al.*, 1998):

Table 1 Advantages and disadvantages of material combinations

Type of material combination	Advantage	Disadvantage	Reference
MoM	Wear rates are 20–100 times lower compared to metal-on-conventional polyethylene; good range of movement; lower dislocation rate; preservation of the femoral head and neck	Local bone and soft tissue necrosis, with pseudotumor formation; cobalt and chromium ions have been detected in the body	(Merola and Affatato, 2019; Silva <i>et al.</i> , 2005; Hu and Yoon, 2018; Willert <i>et al.</i> , 2005)
MoP	Good long term results in elderly patients	High wear rates; aseptic loosening; hip dislocation	(Merola and Affatato, 2019; Hu and Yoon, 2018)
CoP	Low fracture rates; low wear rates.	Risk of alumina head fracture;	(Hu and Yoon, 2018)
CoC	Biologically inert; good lubrication properties; low wear rates	Squeaking noise of ceramic bearings; ceramic head fracture	(Haq <i>et al.</i> , 2012; Hu and Yoon, 2018)

Note: Hu, C.Y., Yoon, T.R., 2018. Recent updates for biomaterials used in total hip arthroplasty. *Biomaterials Research* 22 (1), 33.

- (1) Low coefficient of friction.
- (2) Small volume of wear particle generation.
- (3) Low tissue reaction to wear particles.

The most significant development of THR procedure was the use of metal on high-density polyethylene as a bearing surface. However, polyethylene debris led to osteolysis and aseptic loosening of the prosthesis (Kumar *et al.*, 2014). The significant amount of research has been focused on trying to develop an alternative bearing surface with lower amount of particulate debris.

For the acetabular side of the bearing, ultra high molecular weight polyethylene (UHMWPE), highly crosslinked UHMWPE, metal alloys and ceramics are used, while for the femoral side of the bearing metal alloys and ceramics are used. UHMWPE is a polyethylene with good properties, such as extreme hardness and durability, good chemical resistance, abrasion resistance, very low coefficient of friction, being easy to fabricate. The main limitation of UHMWPE is the small size of wear debris shed which cause adverse reaction to the surrounding tissue (Shahemi *et al.*, 2018). Highly crosslinked UHMWPE demonstrated superior wear resistance during in vitro tests compared to UHMWPE. Advances in the field of polymer manufacturing have been able to reduce wear by at least 50% compared to conventional polyethylene (Dumbleton *et al.*, 2006). Nevertheless, further improvements are desirable in order to additionally reduce the wear rates.

The advantage of using ceramics for the femoral head is in its ability to make the surface smoother, which results in lower friction coefficient and more optimal wear characteristics. Ceramic heads are harder and more chemically stable compared to the metal ones. Advantages and disadvantages of these material combinations are given in Table 1.

Ceramic-on- polyethylene has become one of the most popular bearing surfaces due to studies indicating that it reduces wear rates compared cobalt-chrome heads on polyethylene. Although, the wear rates are reduced, the wear still occurs (Lombardi *et al.*, 2010). In order to reduce polyethylene wear, ceramic-on-ceramic bearing surfaces were introduced. Even though the new advances in the development of ceramics increased the number of ceramic-on-ceramic bearing surfaces, clinical studies have shown no difference between CoC and CoP bearing surfaces during the first five years of implant usage (Rieger, 2001).

The femoral stem is the load-bearing part of the hip implant. In order to avoid the stress shielding, femoral stem material should have a Young's Modulus comparable to the modulus of cortical bone (Mirza *et al.*, 2010). If the material is stiffer than bone, stress shielding will occur. This difference can lead to more loading of the implant than the bone, which results in the bone cells death over time (Adamovic *et al.*, 2018). The stress shielding leading to bone resorption. In the case of uncemented fixation type, the surface of femoral stem is porous which allows the bone to grow and better connect to implant. Usually, this part of the implant is built from titanium and its alloys, but stainless steel, cobalt-chromium alloys can be used (Merola and Affatato, 2019).

The focus in the field of biomaterials for hip implants is toward mechanical strength, bioactivity, better wear resistance and mechanical reliability (Hu and Yoon, 2018).

Ceramic and Composite Biomaterials

Composite Biomaterials

Composite materials are made by combining at least two materials with different properties in order to create a material with great combination of hardness, strength, plasticity and toughness. An important characteristic of composite material is that each component retains its properties (chemical, physical, and mechanical) (Affatato *et al.*, 2015). Some advantages of composite materials are low cost production, high specific strength and stiffness, complex shapes and flexible design and corrosion resistance (Iftekhar, 2004). A composite material consists of two phases: discontinuous phase and continuous phase. The continuous phase (matrix) is responsible to protect the discontinuous phase (permanent or degradable reinforcements) from a variety of external influences (Adamovic *et al.*, 2018). For the composite matrix, polymer (e.g., polyethylene, polyurethane, polyether-ether-

ketone, polysulfone), metal (e.g., stainless steel, cobalt-chrome and titan compound) and ceramic (based on Al_2O_3 , ZrO_2 or HAp) matrix are used. Reinforcements used for composite biomaterials are polymers (i.e., carbon, glass, aramid), metals and ceramics (Chawla, 2013). Ceramic reinforcements have been mainly used for the shaping of particles, as they are too brittle to be used as fibers (Adamovic *et al.*, 2018).

Considering the application in medicine, ceramic and metal matrix have been rarely used compared to a polymer matrix. However, this has been changing in the past years, and ceramic matrix composites (CMCs) are a good example of this as CMCs consist of ceramic fibers and ceramic matrix. The main advantages of CMCs are high strength at high temperatures and low weight (Barros *et al.*, 2018).

Ceramic Biomaterials

A ceramic is a material that contains both metallic and non-metallic elements in order to form complex compounds and solid solutions such as SiO_2 , ZrO_2 , Al_2O_3 and SiC . Metallic and non-metallic elements are bonded with ionic and covalent bonds. Ceramic biomaterials (bioceramics) are mostly used in orthopedics for scaffolds, bone substitutes, and for implant coatings to provide biocompatibility (Adamovic *et al.*, 2018). They have been used for hip replacement for more than 30 years as they have been able to reduce the wear rate in the THR (Affatato *et al.*, 2018). The low wear rate is the result of high hardness of alumina ceramics (Burger and Richter, 2001).

Bioceramics can be classified into four types (Raković and Uskoković, 2010; Adamovic *et al.*, 2018):

- (1) Inert (Al_2O_3 , ZrO_2): does not form bonding with the bone instead create fibrous layers to prevent implant dislocation during functioning.
- (2) Porous (HAp, HAp coating): create bonds that can endure great mechanical loads through tissue ingrowth into the pores and voids.
- (3) Bioactive (bioactive glass, bioactive glass-ceramics and thick calcium-phosphate ceramic): promote specific tissue response to the implant surface to enhance bonding between them; enhance active chemical reactions with tissue by creating an apatite layer on the implant's surface that is similar to bone tissue.
- (4) Degradable (calcium-phosphate): gradually disappear over time and are simultaneously replaced by newly formed tissue – calcium-phosphate.

The advantages of bioceramics are excellent biocompatibility, mechanical resistance, low wear rates, good thermo-mechanical and tribological properties and good corrosion resistance (Affatato *et al.*, 2018). The main disadvantages are poor mechanical characteristics of calcium-phosphate-based bioceramics, low resistance to fracture, very brittle (Al_2O_3), difficult to fabricate (Adamovic *et al.*, 2018), susceptible to slow crack growth (De Aza *et al.*, 2002).

Alumina and zirconia are the most used ceramic in the orthopedic field. Properties of alumina ceramics are high hardness, wear resistance, chemical stability (Affatato *et al.*, 2018). The main disadvantage of alumina is weaker mechanical resistance (Merola and Affatato, 2019). Alumina has been used for THR implants since 1970s, when it was noticed that it provides good clinical results. This was the first-generation ceramic. However, this alumina was different than the first generation used for industrial applications which had low density and large grain size (Merola and Affatato, 2019). The problems with the alumina used in the 1970s were high rate of implant fractures, femoral head and socket fixation, aseptic loosening of the acetabular component (Hannouche *et al.*, 2018). Once the fracture starts, it progresses very rapidly, without previous plastic deformation (Piconi *et al.*, 2003). Advances in the manufacturing technology allowed for development of alumina ceramics with greater density, lower porosity, and increased fracture strength (Kurtz *et al.*, 2014). The alumina ceramics developed after the 1977 belongs to the second-generation (D'Antonio and Dietrich, 2006). The third-generation alumina ceramics have been able to exceed the survival of the conventional implants in patients who are under 50 years of age. The third-generation has an excellent wear performance with inert debris, decreases the possibility of dislocation and osteolysis in the long term (Hannouche *et al.*, 2018).

Zirconia ceramics have been introduced as a way to potentially improve the mechanical strength of the ball for THR. It has shown to be a good alternative to alumina, as high specific strength and toughness of zirconia are able to reduce the risk of fracture (Affatato *et al.*, 2015). Zirconia has been used for femoral heads since 1985 (Piconi *et al.*, 2003). At first, researchers have tried to partially stabilize zirconia with magnesia. Unfortunately, obtained material was not able to provide good wear resistance (Rahaman *et al.*, 2007). After that, the research was dedicated toward the use of yttria stabilizing oxide (Y-TZP), which is the current standard. Yttria stabilizing oxide consists of tetragonal grains with size less than 0.5 μm . Y-TZP has excellent wettability properties, which allow the film formation between the bearing surfaces. The biggest problem with zirconia is that it is prone to aging when exposed to water (Merola and Affatato, 2019).

We are currently on the fourth generation of ceramics that consists of consist of alumina and yttria-stabilized tetragonal zirconia nanosized particles, known as alumina matrix composite (Lombardi *et al.*, 2010).

Ceramic Matrix Composites

Wide application of ceramics has been limited by ceramic fractures and the higher implant cost (Lee and Kim, 2017). Alumina ceramics have been used due to its hardness, stiffness and corrosion resistance, while Yttria Tetragonal Zirconia Polycrystal (Y-TZP)

has found application due to its superior strength (Burger and Richter, 2001). Even though, the third-generation pure alumina ceramics was shown to be safe and to provide long-term results, there were some concerns with fractures, squeaking noise, impingement (Baek *et al.*, 2015). As a result, improved ceramic materials such as alumina matrix composites have been developed. Alumina matrix composite (AMC) consists of an alumina matrix and homogeneously distributed zirconia nanosized particles that serve as the reinforcement. Clinical short-term studies have shown promising results in areas where there were problems with third-generation pure alumina ceramics.

CMCs have been developed to overcome the brittleness and low reliability of traditional ceramic materials. Although they have similar stiffness and hardness as third-generation alumina ceramics, AMCs have almost double the strength and the toughness which reduces the possibility of the fractures (Hannouche *et al.*, 2018). The optimization of manufacturing processes has enabled engineers to develop alumina matrix composite (82% of alumina and 17% of zirconia oxide nanoparticles added to alumina matrix) which combines good characteristics of alumina ceramics (stability, biocompatibility and low wear) with improved mechanical resistance (compared to the alumina) in order to create a potentially more flexible alternative to the traditional alumina for hip prostheses (Masson, 2009). Engineers have been able to increase the material's resistance to flexion by reducing the average size of the grains from 4.5 μm (alumina ceramics) to 1.5 μm (alumina matrix composite). As a result, bending strength has been increased from 400 MPa (alumina ceramics) to more than 1000 MPa (alumina matrix composite) (Masson, 2009). The introduction of zirconia up to 25 wt% into an alumina matrix creates a class of ceramic materials that are known as Zirconia Toughened Alumina (ZTA). Submicron-size Yttria Tetragonal Zirconia Polycrystal grains are finely and evenly dispersed within the alumina matrix which leads to high fracture toughness, strength and reliability but also to significant aging (Piconi *et al.*, 2003). The role of zirconia nanosized particles is to prevent crack propagation (Kurtz *et al.*, 2014). If a crack occurs, it will propagate towards the less rigid Zr grains, which will lead to a phase transformation of the particles. They will transform to monoclinic phase from the stable tetragonal phase, which results in a slight increase in volume. As a result of this transformation, the density will increase, which creates compressive forces near a crack tip and limits the growth of the crack (Hannouche *et al.*, 2018). However, alumina matrix ceramics have their weak point such as the transformation from tetragonal crystalline phase to monoclinic phase happening, even under physiological conditions due to the presence of biological fluids and frictional heating (Arita *et al.*, 2015). This alters the integrity of the material and increases surface roughness, and potentially reduces sliding properties over time (Hannouche *et al.*, 2018).

CMCs have found their application as the bearing surface of the artificial hip joint. The ideal bearing surface should meet the following criteria (Affatato *et al.*, 2018): able to tolerate high cyclic loading for several decades, good biocompatibility, corrosion and wear resistance, bioinert, durable.

The first ZTA material used for hip replacement was introduced under the name BIOLOX® delta (Gadow and Kern, 2010). It is obtained by three chemical-physical reactions where these reactions are responsible for (Affatato *et al.*, 2015):

- (1) Reaction 1: increasing the hardness and the stiffness of the alumina matrix.
- (2) Reaction 2: increasing the hardness, strength, fracture toughness, and reliability of the ceramic due to the platelet formation.
- (3) Reaction 3: high fracture toughness, strength and reliability are obtained as a result of the formation of submicron-size YeTZP grains that are finely and evenly spread within the alumina matrix.

Although, alumina matrix composites have shown improvement in wear rate compared to alumina ceramics, one problem that has been noticed is that zirconia aggregates leading to aging sensitivity (Deville *et al.*, 2003; Gutknecht *et al.*, 2007). The factors that influence in vivo aging are complex and not completely known. However, biological environment is an important factor in this process (Horie *et al.*, 2017). The results obtained by accelerated aging (up to 20 h) that was conducted in order to better understand the role of alumina grains on zirconia phase stability and mechanical equilibrium in AMC head during the aging processes in a clinically-relevant time frame (up to 40 years) indicate that the presence of stable and hard alumina in the AMC can play a considerable role in aging resistance which is yet to be confirmed by clinical studies (Horie *et al.*, 2017). Their goal was to analyse interaction between the AMC femoral head and aqueous environment. For the analysis, the material consisting of an alumina matrix (82%) reinforced by yttria-stabilized zirconia (17%), chromium oxide (0.5%) and strontium aluminate (0.5 vol%) was used. To stabilize the tetragonal structure of zirconia, 1.3-mol % yttria (Y₂O₃) was added, while chromium oxide (Cr₂O₃) and strontium oxide (SrO) were added to increase hardness. Beside increasing the hardness, Cr₂O₃ also improves protective role of alumina (Pezzotti *et al.*, 2010).

One of the reasons, CMCs were introduced was to reduce the wear and fracture rates. Clinical follow-up studies of the AMC femoral heads performed so far, have reported low wear rates and low incidence of fracture after primary THA (Lombardi *et al.*, 2010). Lee and Kim (2017) have analysed almost 6 million femoral heads (3.2 million pure alumina and 2.78 million alumina matrix composite ceramic femoral heads) sold and implanted between January 1, 2000, and December 31, 2013. Although, the modern pure alumina ceramic heads are reliable with low risk of fracture, alumina matrix composite ceramic femoral heads have shown to be even more reliable with 1 in 100,000 (0.0010%) fractures compared to 1 in 5000 (0.0201%) for pure alumina based on the analysis of nearly 6 million femoral heads. According to their research, the majority of the fractures (90%) that did occur happened within 72 months and were results of trauma, hip dislocation or component malposition. Based on the analysis of the ball head size and its reliability, they concluded that smaller ball head (28 mm) size will probably lead to fracture compared to larger ball head size (32 or 36 mm). The increase of the femoral head diameter has been shown to improve hip range of movement, reduce the risk of dislocation (Girard, 2015), reduce the risk of femoral head fractures (Cross *et al.*, 2012). However, the larger diameter size has been connected to the higher incidence of squeaking. Although, the AMC femoral heads have shown lower fracture rates, that was not the case with AMC liners, where the fracture rates were between 1.1% and 3.8% (Hannouche *et al.*, 2018).

One of the disadvantages of ceramic-on-ceramic bearing is the squeaking, with incidence rates being from 1% to 20% (Owen *et al.*, 2014). The incidence rates of squeaking were increased with the introduction of alumina matrix ceramics and it is in range, from 6% to 31% (Hannouche *et al.*, 2018). It is mostly painless, but greatly affects the quality of life (Hannouche *et al.*, 2018). The reasons for squeaking noise are unknown and they are probably depending on multiple factors such as age (Sexton *et al.*, 2011) lubrication problems (Chevillotte *et al.*, 2010), head-neck ratio, stem design and stem alloys (Restrepo *et al.*, 2010), impingement between the acetabular component and the stem (Parvizi *et al.*, 2011). Considering the stem material, it was noticed that squeaking is seven times more likely to happen with the use of titanium-molybdenum-zirconia-steel alloy femoral stems compared to titanium-aluminum-vanadium stems (Restrepo *et al.*, 2010).

There have been attempts to develop an alumina ceramic composite reinforced with Carbon Nanotubes (CNT) (An and Lim, 2002). However, there are significant issues with the agglomeration and dispersion of the CNT inside the alumina matrix.

Conclusion

Total hip replacement is one of the most successful medical procedures. With the number of THRs procedures expecting to be significantly increased in the following decades, further research in this field is necessary. Although, there are several directions in which future research will be oriented, the bearing surface is one of the most important ones. Improved bearing surface will reduce the wear rate, which will improve longevity of hip implants. At the moment, available bearing surfaces are showing promising results, but are unable to completely meet all the requirements of ideal bearing surface.

In the recent years, ceramic and composite materials have found more application in medicine, especially in the orthopedic field. By combining alumina ceramics and Y-TZP, engineers were able to develop a superior biomaterial with that combines the best properties of alumina and zirconia ceramics. Currently, the obtained short-term results are showing promising results for application of CMCs for hip implants. Their properties such as good biocompatibility and wear rate makes CMCs good choice for use in the orthopedics field. However, in order to better understand the effects of new materials on implant longevity and human health, long-term clinical studies are needed to provide information regarding their safety and superiority. As clinical studies require a lot of time, one possibility to get insight into material behavior is through computational models. The use of computational models can provide important information in a short time period and compare the results under different conditions which can be problematic during clinical studies.

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Application of Ceramic Matrix Composites in Drug Delivery Systems

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Glossary

Bioactive material Material that can induce specific biological activity.

Biodegradation Destructive process which involves transformation of a substance into new compounds through chemical (hydrolysis or oxidation) or biochemical reactions (enzymatic cleavage) or the actions of microorganisms.

Ceramics Complex compounds and solid solutions formed by the application of heat, or heat and pressure, composing metallic and non-metallic elements, bonded to each other by ionic and covalent bonds.

Coating Functional covering applied to the surface of an object.

Composite Combination of at least two different materials in which the reinforcing phase is embedded in the matrix phase.

Drug delivery system Formulation which controls the rate and period of drug delivery, and targets specific areas of the body.

Scaffold Structure that allows cells and extracellular-matrix to interact, and provides mechanical support for growing cells and tissues.

Introduction

Biomaterials are most common materials used to repair or replace damaged parts of the human body. They can be categorized as inorganic (metals and ceramics) and organic (polymers) (Adamovic *et al.*, 2018). In order to satisfy specific application and desired properties, the single-classes biomaterials have to be combined. Composites are defined as combinations of two different materials to achieve enhanced biocompatibility and biomechanical properties, in which the reinforcing phase (fibers, sheets, or particles) is embedded in the other phase called matrix phase. Generally, both reinforcing and matrix phase can be either metal, ceramic or polymer. Depending on specific application of drug delivery systems (DDS), the reinforcing phase can be drugs, growth factors, bioactive biomolecules, etc.

Ceramics can be defined as complex compounds and solid solutions formed by the application of heat, or heat and pressure, composing metallic and non-metallic elements, bonded to each other by ionic and covalent bonds (Adamovic *et al.*, 2018). Development of different types of ceramics that is biocompatible and bioactive (i.e., bioceramics) have increased its utilization in the biomedical and pharmaceutical sciences, due to ability to bond with the host living tissues. Advanced fabrication techniques and chemical processing enabled creation of DDS based on bioceramics as a drug carrier. This article provides a general overview of ceramic matrix composites (CMC) in DDS, discussing different types of bioceramics, such as calcium phosphate (CaP) ceramics, CaP cements and bioactive glasses. Considering different architectures of drug carriers, a general overview is given for CaP coatings, CaP scaffolds and CaP particulates. The discussion is further focused on ceramic/polymer composites in DDS. Finally, ceramic nanocomposites with application in targeted drug delivery are briefly presented.

Ceramics in Medical Application

Different composition, structure and properties of musculoskeletal system require application of tailored and sophisticated biomaterials, when comes to musculoskeletal diseases and disorders. Both inorganic and organic biomaterials, have found specific applications in tissue engineering. Among different options, bioceramics, such as CaP ceramics, cements and silica-based glasses, is found to be attractive choice, due to its excellent biocompatibility, as well as customizable bioactivity and biodegradability. The CaP systems are increasingly being explored as DDS for numerous applications in orthopedics, dentistry and nanomedicine (Veron *et al.*, 2010).

Nevertheless, the high density and slow biodegradability of ceramics is not beneficial for tissue engineering purposes. To address these issues, macroporosity can be introduced in combination with osteoinductive growth factors and cells. Ceramics is good drug carrier, in which release patterns depend on the chemical consistency of the ceramics, type of drug, as well as drug loading. Also, biodegradable polymers are widely used as matrices or additional elements that introduce a tailored biodegradation/drug release to the ceramic material.

CaPs are used as carriers of various growth factors, bioactive biomolecules, and drugs to induce osteoinductivity in the implanted biomaterials and to accelerate the healing process in bone tissue engineering (Arcos and Vallet-Regí, 2013). In recent paper, Parent *et al.* (2017) reviewed the parameters affecting the loading and release of the therapeutic substance, related to the design of CaP ceramics for drug delivery in bone diseases. There are many studies examining the use of CMC composites for

controlled release of antibiotics and other drugs (Habracken *et al.*, 2007; Simchi *et al.*, 2011). More specifically, CaPs have been widely studied as carriers of antibiotics (e.g., gentamicin sulfate, flomoxef sodium, tetracycline, etc.), anti-inflammatory agents (e.g., salicylic acid, indomethacin), analgesic and anticancer drugs (e.g., mercaptopurine, estradiol), growth factors (e.g., bone morphological proteins, transforming growth factors β (TGF- β), etc.), proteins (e.g., collagen I and osteocalcin) and genes (e.g., DNA), due to their biocompatibility, bioabsorbability and bioactivity (Ginebra *et al.*, 2006).

In nanomedicine, CaP nanocarriers are widely used in tumor diagnosis, gene delivery, drug delivery and theranostics (Huang *et al.*, 2019; Kaurav *et al.*, 2018). Also, nanocomposites in DDS are applied in tissue engineering and bone regeneration (Amler *et al.*, 2014). In addition, nanocomposites with ceramic coatings have been applied in diagnosis and treatment of atherosclerotic coronary artery (Karimi *et al.*, 2016). Such an approach can be combined with computational modeling of atherosclerosis (Djorovic *et al.*, 2019a,b; Robnik-Šikonja *et al.*, 2018) for further technological advancements by merging different methodologies.

From the economic point of view CaPs can be produced in large quantities, against relatively low cost, they are stable and therefore available for different medical applications. On the other hand, their use is also associated with drawbacks, such as poor mechanical properties, thus the incorporation of reinforcing elements is needed. This, however, does not reflect the enormous diversity of CaPs both in terms of products and their applications (Habracken *et al.*, 2016).

Drug Delivery Systems

DDS present a prospective for improving the therapeutic efficiency of the existing drugs. DDS can be described as a formulation which controls the rate and period of drug delivery, and targets specific areas of the body. The engineered DDS are either targeted to a particular location or are intended for the controlled release of therapeutic agents at a particular site. The design and development of DDS with both controlled release or targeted delivery of bioactive molecules rapidly grow in biomedical and pharmaceutical fields in order to achieve desired therapeutic levels for pre-determined durations, and with limited side-effects. Enhanced therapeutic efficiency of DDS requires simultaneous consideration of several factors. Efficient DDS deal with type of drug carrier, drug characteristics, targeting ability, administration route, drug release mechanism, biocompatibility, delivery duration and drug bio-availability. Developed DDS which successfully address all of these challenges will have advantages in reduced side-effects, improved efficacy of the existing drugs and established basis for new class of medical treatments.

There are a number of DDS successfully employed in the recent time. The application of biocompatible ceramics in DDS offers new possibilities and overcomes problems found in traditional DDS. Bioceramics, such as CaP ceramics, cements and silica-based glasses, is widely used in bone tissue engineering over the last few decades (Paul and Sharma, 2003; Wilson *et al.*, 1993; Zhang and Zhang, 2002). The advanced processing methods and new chemical techniques allow the incorporation of drugs within CaP-based ceramics or on its functionalized surfaces, enabling treatment of large bone defects, osteoporotic fractures, bone infections and bone tumors (Arcos and Vallet-Regí, 2013). Nowadays, certain challenges are addressed and advanced technologies are in development for successful delivery of drugs to its target sites. Hence, the nano based DDS are currently being studied that will facilitate the systems of drug delivery (Patra *et al.*, 2018).

Ceramics as Matrices for Drug Delivery

During the past decades, bioceramics and, more specifically ceramic composites, have supplied successful solutions to different hard tissue disorders (e.g., bone) and soft tissue treatments (Wilson *et al.*, 1993). Ceramics comprised of CaPs, silica, zirconia, alumina, and titanium dioxide are used for different medical applications due to their bioactive effects on human tissues. The current biomedical applications of CaP-based materials include bone reconstruction (LeGeros and LeGeros, 2008), coating of orthopedic implants (Xiao-Ming *et al.*, 2014), dental applications (Al-Sanabani *et al.*, 2013), and drug delivery (Paul and Sharma, 2003; Zhang and Zhang, 2002).

Among ceramic composites, bioactive CaPs and bioactive glasses have been widely used as matrices for drug delivery. In the last four decades, a high biocompatibility and the positive biological effects of their reaction products after implantation have made CaP and silica-based glasses into the most interesting bioceramics. Both CaPs and bioactive glasses can be produced by different synthesis approaches (high-temperature methods, controlled precipitation and the sol-gel process). The final form of the materials can be as powders, granules, dense pieces, coatings and porous scaffolds, providing a wide range of solutions for specific clinical use (Arcos and Vallet-Regí, 2013).

In general, from dimensional perspective and architectural point of view, the CaPs can be differentiated as particulates (0D), coatings (2D structure) and scaffolds (3D structure). The graphical presentation of ceramic composites that are discussed in this article together with their application in DDS is given in Fig. 1. It should be noted that the CaPs comprise a variety of compositions characterized by their Ca/P molar ratio: the lower the Ca/P ratio, the faster the CaP biodegradation. Also, drug delivery can vary depending on whether it is a NP, coating, scaffold, ceramics, cement or glass. NPs only can have targeted drug delivery, while other CaPs have local delivery.

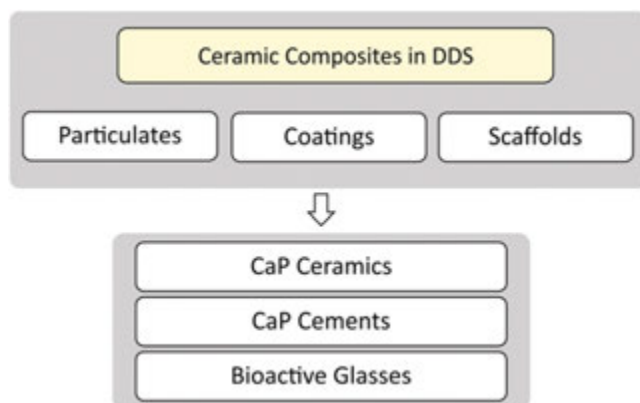


Fig. 1 Ceramic composites in DDS.

Calcium Phosphate Ceramics

CaPs such as ceramics, particulates, scaffolds and coatings have attracted significant interest for drug, protein, and growth factor delivery toward different clinical applications. CaP ceramics can be classified as follows: hydroxyapatite (HA), beta-tricalcium phosphate (β -TCP), biphasic calcium phosphate (BCP), amorphous calcium phosphate (ACP), carbonated apatite (CA) and calcium deficient HA (CDHA). CaP systems, including HA and TCPs, possess variable stoichiometry, functionality and dissolution properties which make them suitable for delivery of biomolecules/drugs. Their chemical similarity to bone and thus biocompatibility, as well as variable surface charge density contribute to their controlled release properties and delivery (Verron *et al.*, 2010; Rauschmann *et al.*, 2005).

Among various CaP ceramics, hydroxyapatite [HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] and tricalcium phosphate [TCP, $\text{Ca}_3(\text{PO}_4)_2$] have the most common use in bone tissue treatments, possessing good osteogenic properties, phase stability and ability to form strong bonds with the host bone tissues. HA is well known for its osteoblast attachment and proliferation. On the other hand, major drawback of HA is limited degradation ability in vivo. Also, HA is known as a non-bioresorbable ceramics in contrary to TCP which is bioresorbable, having higher solubility than HA. Ca-deficient or non-stoichiometric apatites (e.g., CA and CDHA) can be resorbable, while pure HA formed at high temperature is nonresorbable. However, complete resorption of HA is very difficult in most cases due to the crystalline architecture. There are different approaches in introducing porosity of CaP-ceramics. Mastrogiamaco *et al.* (2006) used cellulose in combination with HA, applying leaching and sintering to remain porous HA matrix, while Almira *et al.* (2004) performed foaming methods using H_2O_2 as foaming agent to produce porosity inside CaP ceramics.

Due to the positive influence of CaP ceramics on differentiation and proliferation, adding osteo-inductive growth factors/drugs is very successful. In order to examine the release patterns of CaP ceramics, Stallmann *et al.* (2006) added the gentamycin to different CaP granules showing a very low release and considerable amount of the retained gentamycin, while Guicheux *et al.* (1998) added human growth hormone onto a macroporous BCP ceramic showing less than optimal release, but 100% of human growth hormone was released, by remaining both biological activity and structural integrity. In contrary, there are several studies presenting the degradation of growth factors in time (Kimakhe *et al.*, 1999; Ziegler *et al.*, 2002).

Calcium Phosphate Cements

Beside the CaP ceramics, CaP cements are widely used in bone tissue engineering, due to their advantageous properties including bioactivity, osteoconductivity, injectability, moldability and ability to serve as a carrier of drugs and biological molecules (Ginebra *et al.*, 2006). In addition, they can be resorbable, where resorption rate depends on the composition and microstructure. CaP cement is defined as a bioactive and biodegradable grafting material in the form of powder and liquid, which when mixed, lead to hardening of the cement. The powder (inorganic) phase of CaP cement systems consist of dicalcium phosphate (DCP), dicalcium phosphate dihydrate (DCPD), tetracalcium phosphate (TTCP), ACP, calcium-deficient HA (CDHA), carbonate HA, α -TCP, β -TCP, or octacalcium phosphate (OCP), while liquid is usually water or an aqueous solution.

In comparison with CaP ceramics, the main difference of the CaP cement is the injectability and in situ hardening through a body-temperature dissolution-precipitation reaction which sets biocompatible apatite and brushite as end products. The in situ hardening makes it easier for use in clinical practice and represents a clear advantage with respect to CaP ceramics. On the other hand, due to the intestine porosity of CaP cements, their strength is lower comparing with CaP ceramics, while poor mechanical performances limit their adjustability to non- or moderate loadings. Nevertheless, the intestine porosity of CaP cements allows the incorporation of drugs and bioactive molecules, retaining their activity during preparation and implantation process (Ginebra *et al.*, 2012).

In case of drug incorporation into the CaP cements, it can be performed by mixing the drug with the liquid or powder components, adding the drug onto the pre-set scaffold, or into polymeric microspheres or microfibers before blending with

cement paste (Farokhi *et al.*, 2013). In this process the attention must be paid on physicochemical properties of the drug/protein which should not be changed during the chemical reaction and setting of cement. In addition, the incorporation and releasing of drug depend on microstructure of CaP cement, its porosity, surface, loading procedure of drug, as well as the interaction between the drug and matrix of the CaP cement (Parent *et al.*, 2017).

In the clinical practice, various drugs have been incorporated into the CaP cements: antibiotics (Ghosh *et al.*, 2016; Su *et al.*, 2013; Yu *et al.*, 2010), anticancer drugs, such as cisplatin, doxorubicin, paclitaxel, methotrexate, mercaptopurine etc. (Li *et al.*, 2010a; Lopez-Heredia *et al.*, 2011; Tanzawa *et al.*, 2011), growth factors (Blom *et al.*, 2002) and proteins (Walters *et al.*, 2013; Weir and Xu, 2008). Furthermore, CaP cements in combination with tricalcium silicate, hinokitiol or hinokitiol/tricalcium silicate are widely applied as for endodontic materials showing significant antimicrobial and antibacterial behavior (Shieh *et al.*, 2017). A more controlled release, enhanced resorption and degradability, as well as promoted osteogenesis have been achieved by incorporating biopolymers as the second phase of carrier into CaP cements, which mimic more closely the characteristic of bone tissues. Such biopolymers which improve mechanical properties of CaP cements are collagen (Ohara *et al.*, 2012; Perez and Ginebra, 2013), gelatin (Li *et al.*, 2010b), bioactive glass (Nezafati *et al.*, 2011), particles of glucose porogens and poly(lactic-co-glycolic acid) – PLGA (Smith *et al.*, 2018), etc. In general, the release of the pharmaceutical agents from CaP cements is a diffusion dominated process through the matrix.

Although CaP cements as matrices for drug delivery efficiently promote osteogenesis and have excellent applicability, their application is still limited, due to the changes in the properties of CaP cements after drug loading, as well as changes in the drug bioactivity. The potentials and clinical applications of cements in local delivery of drugs are still developing, enhancing their properties and biocompatibility.

Bioactive Glasses

Bioactive glass, commercially called Bioglass(R), refers to the glass compositions with ability of bonding to living tissues. It belongs to group of bioceramics used in bone tissue engineering mainly for stimulation of osteogenesis by inducing a biological response at the biomaterial–bone interface which promotes proliferation and differentiation of human osteoblasts (Dziadek *et al.*, 2016).

In recent study, Karmakar (2017) presented chronological developmental of biomedical glasses and glass-ceramics in period 1971–2011, as well as a more detailed described the following diversities:

- (1) Bioactive glasses;
- (2) Bioactive glass-ceramics;
- (3) Bioactive glass composites;
- (4) Bioactive glass coatings;
- (5) Antibacterial and drug delivery bioactive glasses;
- (6) Radioactive glass microsphere for malignant tumors;
- (7) Nano bioactive glasses;
- (8) Bioactive bulk metallic glasses;
- (9) Glass ionomer cements.

The compounds of silicon, phosphorous, sodium and calcium (e.g., SiO₂, Na₂O, CaO, P₂O₅) are basis for conventional bioactive glass, while presence of both CaO and P₂O₅ is the primary condition for bonding with living bone made up of HA. The chemical reactivity of the bioactive glass in which silicon bonds are broken and a CaP-rich layer is deposited on top of the glass which crystallizes to hydroxycarbonate apatite (HCA) presents the bone bonding ability. Compositions of commercial bioactive glasses such as 45S5 Bioglass (NovaBone) and S53P4 (AbminDent1) (Hench *et al.*, 2010) have excellent ability to degrade in the body fluid, releasing drugs/ions into the medium, and at the same time converting to HA, and bond strongly to bones and soft tissues.

Bioactive glasses are usually created by the melt-quenching synthesis, after which the glass is being converted into the desired shape (particle, fiber, porous 3D scaffold) using standard materials processing techniques (grinding, fiber pulling, or sintering) (Rahaman, 2014). Comparing to conventional bioactive glass produced by melt-quenching synthesis (usually of oxides), the bioactive glass produced by sol–gel synthesis has a finer porous structures and higher bioactivity and bioresorbability (Baino *et al.*, 2018). The sol–gel synthesis as a base has been used for bioactive glasses with small and different morphologies in micro/nano size, such as: powders, coatings, fibers or 3D porous scaffolds (Zheng and Boccaccini, 2017), making them suitable for drug/ions doping and controlled release. Furthermore, the ordered mesoporous structure obtained by sol-gel process represents an alternative to antibiotics in prevention of infections (Kaya *et al.*, 2018). However, the precursor materials used for sol–gel synthesis are usually expensive. The third method for bioactive glass fabrication which is less expensive than sol-gel technique is microwave-assisted synthesis, introduced by Sarkar and Lee (2011). The all three types of bioglass synthesis are detailed explained by Mulchandani and Katiyar (2019).

In the bone tissue engineering, the sol-gel foamed bioactive glasses with incorporated ions showed significant results in antibacterial and antimicrobial processes. In these processes the bioactive glass degrades by releasing ions which induce the antibacterial effects. Recently, the effects of additive ions, such as aluminum (Weng *et al.*, 2018), strontium (Ranga *et al.*, 2019;

Sharifianjazi *et al.*, 2017), copper (Wu *et al.*, 2019), fluoride (Xu *et al.*, 2015), silver (Ranga *et al.*, 2019; Weng *et al.*, 2018) and zinc (Eltohamy *et al.*, 2018) on therapeutic properties of the glasses have been investigated. Among mentioned metallic ions, the zinc and silver raised the highest attention due their optimal bioactivity and antibacterial effects. In the recent comparative study of sol-gel derived 58S bioactive glass substituted by these two metallic ions, the results showed that silver bioglass samples have better antibacterial effect in comparison to zinc bioglass samples (Shahrababak *et al.*, 2019). Beside the application in field of bone tissue engineering, Schuhladen *et al.* (2020) published an interesting study related to examination of additive copper and zinc and their antibacterial effect on specific immune cells (murine dendritic cells). Finally, independently on doped metallic ions, the dissolution rate and the concentration of doped elements affect the antibacterial efficacy. Thus, the balance between antibacterial activity and biocompatibility is required, considering that a high dose of doped metallic ions can lead to cytotoxicity (Newby *et al.*, 2011).

The main disadvantage of bioactive glasses is their brittle and stiff nature restricting them to be molded into complex shapes which frequently leads to the fracture under mechanical loads. Due to nonoptimal mechanical properties of the bioactive glass, the ceramic components are incorporating in order to stabilize the chemical structure, leading to the new vitroceramic state, or glass-ceramics composites. Glass-ceramics is prepared by the well-controlled heat treatment, embedding the nano- and/or micrograined polycrystalline phases in residual glass phase. In general, the glass-ceramic has mechanical properties superior to the parent glass but a lower bioactive potential due to the better stability of the crystalline material.

According to the chronologically presented development of bioactive glasses by Hench (2015), today these composites are in the era of innovation, with major findings in bioglass-derived glass-ceramic scaffolds for bone tissue engineering (Boccardi *et al.*, 2017; de Siqueira *et al.*, 2018). In drug delivery systems, glass-ceramics and glass-ceramics scaffolds have significant role (Jones, 2013). More details about CaP scaffolds including glass-ceramics scaffolds can be found in Section "Calcium Phosphate Scaffolds". However, a high porosity and intrinsic brittleness of glass and glass-ceramic scaffolds affect the mechanical strength and limit their application in case of mechanical loads (e.g., as prosthetic materials). This disadvantage has been overcome by adding the polymers into the glass composition (see Section "Bioglass/Polymer Composites").

Calcium Phosphate Coatings

CaP coatings onto metallic implants have found wide application to initiate a bioactive fixation after surgery, and to increase the long-term activity by incorporating the drug carriers (Xiao-Ming *et al.*, 2014). Knowing that metallic implant has poor osteoconductivity and as foreign body can cause post-operative infections, introduction of 2D bioactive ceramic coating onto implant surface has dual function: as fixation and antibiotic drug carrier. In order to enhance osteoconductivity, growth factors can be applied on CaP-coated implants for bone tissue regeneration (e.g., in dental or orthopedic application) (Pereira *et al.*, 2020).

The effectiveness of implant largely depends on stability and structure of the coating. It is controlled by physical and mechanical properties such as coating thickness and strength, crystallinity, phase composition, dissolution characteristics, etc. The coating techniques such as dip coating, sol-gel, electrophoretic deposition and biomimetic coatings lead to the weak coating strength, while simultaneous vapor deposition, laser processing, pulsed laser deposition and plasma spraying offer advantaged coating strength and crystallinity.

Among various depositing coatings, the outcome of numerous studies has proved that after coating with CaP-based materials such as HA, β -TCP, BCP, etc., implants show enhanced corrosion resistance and increased ingrowth. For example, Prosecká *et al.* (2012) have examined thin-layer of HA coating on a nanofiber poly- ϵ -caprolactone (PCL)/polyvinylalcohol (PVA) surface showing the influence of HA on mesenchymal stem cells stimulation and their differentiation into osteoblasts. Stigter *et al.* (2004) examined release kinetics of antibiotic such as cephalothin, carbenicillin, amoxicillin, cefamandole, tobramycin, gentamicin and vancomycin from carbonated HA coatings, showing that chemical nature and concentration of these antibiotics had a significant influence on the carbonated HA coating thickness formed by the biomimetic technique. In addition, Avés *et al.* (2009) have utilized a sol-gel spin-coating process to coat a titanium alloy with HA and evaluated its efficiency as drug carrier by immersion in gentamicin sulfate. Beside the incorporation of antibiotics into CaP coatings, the metallic ions into CaP coatings have also shown efficacy in antimicrobial in vitro testing (Roy *et al.*, 2009).

As the adsorption of drug or growth factors into CaP coatings is performed after the coating process, this can lead to initial burst release and decreased efficacy of coatings. Nowadays, this drawback is elevated by adding a thin biodegradable polymer coating after drug adsorption, which can be applied in several layers creating layer-by-layer coatings (Park *et al.*, 2018).

Calcium Phosphate Scaffolds

The scaffolds applied in tissue engineering provide mechanical support for new cells and tissues growing during tissue repair. They are usually consisted of polymers (natural or synthetic), bioceramics and hybrid materials (Yang *et al.*, 2017). The microbiological environment suitable for cell survival and function, as well as required biocompatibility of scaffolds affect different designs and manufacturing techniques. The fabrication methods of 3D scaffolds can be conventional, or rapid prototyping (RP)- known as solid free-form fabrication (SFF), each producing scaffolds with different characteristics. In contrary to conventional fabrication methods which are not suitable for scaffolds with complex architectures, SFF techniques allow flexibility in designing and manufacturing of scaffolds with complex geometry. Moreover, the main advantage of SFF is production of customized and patient-

specific scaffolds. Generally, the basic SFF methods include 3D printing (3DP), fused deposition modeling (FDM), selective laser sintering (SLS) and stereolithography (STL) (Abdelaal and Darwish, 2013). Among those SFF methods, the SLS and 3DP are most widely used for ceramic scaffolds fabrication.

Scaffolds based on CaP are usually created using either HA or BCP (composite of HA and β -TCP). CaP-based scaffolds are widely used as they poses biocompatibility, bioactivity, and osteoconductivity. The 3D scaffolds can be found in different shape and pore size, with appropriate porosity and interconnectivity, allowing to newly created tissues to take over the space. Additionally, degradation products can participate in biomineralization by redepositing on HCA (Wang and Nancollas, 2009).

The scaffolds' porosity depends on the solubility of the type of CaP under consideration. The 3D pores of the scaffolds are beneficial to promote cell adhesion and proliferation, mechanical interlocking between host tissue and scaffold, as well as transport of biomolecules. However, due to generally low stiffness and osteoinductivity of scaffolds, the bone tissue engineering scaffolds are usually combined with bone morphogenetic proteins or mesenchymal stem cells. Sun and Yang (2015) reviewed the in vitro and in vivo studies related to the efficiency of CaP-based scaffolds combined with morphogenetic proteins or mesenchymal stem cells, and concluded that both types of composites can repair bone defects more effectively than an autograft.

Different CaP-based scaffolds have been used in bone tissue engineering, whereas bioactive glasses and glass-ceramics attracted great attention due to range of changing either composition, thermal, or processing history. The synthesis and evaluation of glass-ceramics as DDS in osteomyelitis was studied by Thanyaphoo and Kaewsrirachan (2012), showing that vancomycin doped glass-ceramics scaffolds are very suitable for treatment bone diseases including osteomyelitis. In addition, there are excellent reviews in the area of scaffolds based on bioactive glasses and glass-ceramics published by Rahaman (2014); Jones (2013); Gerhardt and Boccaccini (2010); and Fu *et al.* (2011).

In order to improve the stiffness and achieve relatively high porosity and large pore size, which contribute to bioactivity and osteoconductivity of scaffolds, synthetic polymers (e.g., polylactic acid (PLA) and polyglycolic acid (PGA)) and natural polymers (e.g., collagen, glycosaminoglycan, and fibrin) are also widely used (Murphy *et al.*, 2013). Several new hybrid CaP-polymer scaffolds have been developed, including PLGA/CaP cement (He *et al.*, 2013), CaP cement-fibrin glue (Dong *et al.*, 2013), CaP cement-chitosan (Moreau and Xu, 2009), etc. More details about different ceramic/polymer composites are available in Section "Ceramic/Polymer Composites for Drug Delivery".

Calcium Phosphate Particulates

Particulate drug carriers (as opposite to 2D coatings or 3D scaffolds) have various advantages for use in drug delivery, and today, they are probably the most common ceramic DDS. Particulate carriers can efficiently transport drugs through blood vessels, cell membranes, etc., thanks to large surface area-to-mass ratio which affects prolonged drug release. Furthermore, fabrication process and production of particulates are easy to perform, which is suitable for mass manufacturing. Fabricated ceramics whose particle sizes are within the range of 1 nm to 100 nm (i.e., < 100 nm) belongs to nanoceramics and relies on nanotechnology (see Section "Ceramic Nanocomposites for Drug Delivery").

Among different forms of CaPs, TCP and HA are the most common phases that have been used in particulate form in DDS. TCP has three distinct polymorphs, β , α and α' , where the α' has no interest as it transforms into the α form during the cooling process. β -TCP has excellent biocompatibility and osteointegration characteristics, as well as the time-dependent mechanical and dissolution properties suitable for controlled drug release (Banerjee *et al.*, 2010). Similarly, the HA has been used in delivery of genes, proteins, different drugs, due to nontoxicity and excellent biocompatibility.

The CaP particulates are widely used in composites in order to achieve appropriate material characteristics and biocompatibility. The adsorption of biomolecules onto the surface of CaP-based materials depends on the structural properties such as microstructure, surface area, and porosity. The incorporation of nanosized pores in CaP-based materials increases the total surface area and improves integration of biomolecules and drugs within the particles. In addition, more details about nanocomposites can be found in Section "Ceramic Nanocomposites for Drug Delivery". CaP nanoparticles which combine drug delivery, imaging and targeting capabilities still have to be improved, but in general, they are more convertible than metallic nanoparticles (possessing a solid core and an unknown rate of biodegradability), or polymeric nanoparticles (consisting of non-biological compounds) (Habracken *et al.*, 2016).

Ceramic/Polymer Composites for Drug Delivery

Today, it is hard to imagine application of ceramic materials without incorporated additional elements. The ceramic material alone has several disadvantages, such as poor degradability and inadequate mechanical properties (tensile strength and brittleness). From previous sections can be concluded that ceramic based matrices require incorporation of additional elements in order to improve mechanical properties, as well as achieve suitable porosity and controlled delivery of drugs. The addition of biodegradable polymers can improve the degradability of the CaP-based matrices and alter their mechanical and physical properties. Polymer coatings on CaP ceramic matrices are usually incorporated in order to improve weak strength and brittleness. Depending on the added polymer which affects degradation rates and mechanisms, drug release profiles can be alerted. In DDS, controlled drug release is usually achieved with polymer coatings applied to the drug-adsorbed surface of the ceramic scaffolds. Xue *et al.* (2009) presented controlled protein delivery from β -TCP scaffolds with improved strength due to PCL polymer coating.

It should be noted that composites of CaPs and polymers have numerous variations, where both can be either matrices or incorporated elements. As we are focusing on ceramic–polymer composites, there are many studies examining their use for the controlled release of antibiotics and other drugs (Habraken *et al.*, 2007; Simchi *et al.*, 2011). Polymers widely used in combination with ceramics can be divided into following groups (Habraken *et al.*, 2007):

- (1) Polylactic/polyglycolic acid: Polylactic acid (PLA, PLLA, PDLLA), polyglycolic acid (PGA), PLGA, PCL;
- (2) Proteins: Collagen, gelatin, fibrin, casein, peptides;
- (3) Carbohydrates: Chitin, chitosan, cellulose, starch, alginate, hyaluronan, hydroxymethylpropylcellulose (HPMC), amylopectin;
- (4) Other polymers: Poly(propylene fumarate) (PPF), polycarbonate, polyalkanoates, poly(1,8-octanediol-citrate) (POC), poly(ethylene glycol) (PEG), poly(ethylene imine) (PEI), poly(ethylene oxide) (PEO), polypropylene (PP), nylon, aramide, poly(allylamine hydrochloride) (PAH);

Cement/Polymer Composites

In case of CaP cements, their mechanical properties (i.e., strength) are usually increased, together with controlled degradation, by adding polymers (Durucan and Brown, 2000). In order to increase macroporosity of CaP cements, introduction of biodegradable microspheres, such as collagen (Ohara *et al.*, 2012; Perez and Ginebra, 2013), gelatin (Li *et al.*, 2010b) and PLGA (Smith *et al.*, 2018) is usually performed. Composites of gelatin/collagen with CaP cements are formulated to obtain better handling properties and to improve the biological response. Release properties of the collagen/cement composites were investigated by Lode *et al.* (2007). They performed comparative study and examined release of vascular endothelial growth factor (VEGF) from cement alone and collagen containing cement, showing that both cumulative and burst release of VEGF was higher from the collagen cement than from the alone one.

In drug delivery systems, incorporation of polymer in the CaP cement matrix can be performed by adding the drug onto the pre-set scaffold, or into polymeric microspheres or microfibers before blending with cement paste (Farokhi *et al.*, 2013). The effects on drug release kinetics depending on its molecular weight, solubility, degradation rate, and drug–polymer interaction. In antibacterial and antimicrobial application of CaP cements, polymer additives are incorporated to control drug release in its local delivery. For example Bohner *et al.* (2000) added poly(acrylic acid) (PAA) to control gentamicin sulfate (GS) release from CaP cements for local drug delivery. Also, Fullana *et al.* (2010) investigated influence of low-methoxyl amidated pectins (LMA) polysaccharide on the CaP cement properties, as well as ibuprofen (a non-steroidal anti-inflammatory drug) release ability and final macroporosity after microspheres degradation.

Bioglass/Polymer Composites

In bone and musculoskeletal tissue engineering bioactive glass can be present as a dispersed particulate phase (or fiber) incorporated in a biodegradable polymer (e.g., PLA, PGA, PLGA, collagen) or hydrogel matrix (e.g., chitosan, PEG-based). In contrary, bioactive glass can be present as a matrix in form of porous 3D scaffold with incorporated biodegradable synthetic polymer (e.g., PLA, PGA, PLGA) or ceramic/metal particles (e.g., ZrO₂, Ti). The composition of bioactive glass-polymers is more commonly achieved by incorporating bioactive glass particles (or fibers) within the polymer matrix, considering that creation of porous bioactive glass scaffolds with the appropriate shape for bone and tissue engineering is far more challenging comparing with polymer scaffolds (Rahaman, 2014; Rezwan *et al.*, 2006). A general review on bone tissue engineering scaffolds based on composites with inorganic bioactive fillers has been published by Rezwan *et al.* (2006).

In case of bioactive glass as a porous 3D scaffold, its brittle mechanical response can be modified and improved by incorporating the biodegradable synthetic polymers, such as PLGA (Gerhardt and Boccaccini, 2010), polyhydroxybutyrate (Li *et al.*, 2014), PLA or PCL (Xiao *et al.*, 2017). These bioactive glass-polymer scaffolds are promising implants for bone healing, showing a high compressive strength, high flexural strength and a high work of fracture that leads to non-brittle mechanical response (Xiao *et al.*, 2017).

Beside coating the bioactive ceramics and glass with polymers to reinforce the scaffolds structure, the polymer coating has been also used in order to add a drug delivery function to the scaffolds (Philippart *et al.*, 2015). In addition, Araujo *et al.* (2017) recently examined bioactivity, mechanical properties and drug delivery ability of bioactive glass-ceramic scaffolds coated with melanin (a natural-derived polymer) and loaded with ibuprofen. The study showed positive influence of melanin on the scaffolds, in terms of increased bioactivity and initial compressive strength, while ibuprofen was successfully loaded on the scaffolds, allowing a controlled drug release of the anti-inflammatory agent. Although significant studies and improvements have been achieved in the tissue engineering, fabrication of scaffolds with local drug release ability is still highly demanding due to inflammatory responses and delayed bioactivity.

Ceramic Nanocomposites for Drug Delivery

In recent years, development of nanocomposites has increased their application in the biomedical and pharmaceutical fields, enabling controlled and targeted drug delivery. The nanocomposites are new generation of engineering materials which have at least one phase in nano dimension. Similar to nanomaterials in general, nanocomposites have various and unique properties, suitable for drug release applications, such as high specific surface area, improved chemical reactivity, controlled drug release, high

mechanical durability, together with biocompatibility, customizable biodegradability, and non-toxicity (Li and Xia, 2018). Recently, Huang *et al.* (2019) reviewed the advances in the preparation strategies of CaP nanocarriers and their application in tumor diagnosis, gene delivery, drug delivery and theranostics.

According to the different matrices and reinforcing components, nanocomposites can be differentiated as follows: metal matrix nanocomposites; ceramic matrix nanocomposites; polymer matrix nanocomposites; polymer nanocomposites with layered silicates; polymer - nanofiber/carbon-nanotubes/graphene-oxide nanocomposites; biopolymeric nanocomposites; nanocomposites hydrogel; layered double hydroxide (LDH) nanocomposites (Hamadneh *et al.*, 2016; Kaurav *et al.*, 2018). Focusing on ceramic matrices, the common fabrication methods used for ceramic matrix nanocomposites are: conventional powder method, polymer precursor route, spray pyrolysis, and chemical methods (sol-gel process, colloidal and precipitation approaches and template-assisted synthesis) (Camargo *et al.*, 2009). Types of ceramic matrix nanocomposites are $\text{Al}_2\text{O}_3/\text{SiO}_2$, SiO_2/Ni , $\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{Al}_2\text{O}_3/\text{SiC}$.

According to the architecture, nanoceramics can be differentiated into two general categories: nanoparticles and nanoscaffolds, that are still in the development phase.

Ceramic nanoparticles for drug-delivery and antibacterial application are widely used in forms of CaP, iron oxides, silica, titania, alumina, calcium carbonate, and layered double hydroxides (Yang *et al.*, 2010; Sampath Kumar and Madhumathi, 2014). The structural features of CaP nanoparticles, as the most used ones, are: hollow apatite nanospheres, apatite nanocrystals and nanocomposites, with application in controlled on-off drug release (Cai and Tang, 2008), enhanced protein adsorption (Dai and Shivkumar, 2008) and gene transfer (Shen *et al.*, 2004). In targeted drug delivery, magnetic iron oxide nanoparticles (ION) have been biochemically modified to bind to target cells, or subjected to external measures (e.g., magnetic field) to move them to the pathological sites. This technique has found very successful application in tumor imaging and therapy (Yu *et al.*, 2012). Also, the HA nanoparticles (n-HA) have been recently applied in tumor-associated bone segmental defects, assessing the translational value of n-HA both as a bone-regenerating material and as an antitumor agent (Zhang *et al.*, 2019).

Comparing with polymers, ceramic nanoparticles usually have longer biodegradation (or even close to nondegradable) and show more stable behavior in case of changeable pH or temperature. Most important, ceramic nanoparticles have the same chemistry, crystalline structure and size as the constituents of host tissues. Unlike polymers, the ceramic nanoparticles can be improved with electrical, mechanical, optical, or magnetic properties that provide their multifunctionality.

Development of sophisticated scaffolds on nanoscale is of high importance, because various tissues have nanoscale architectures (e.g., collagen fibers and CaP crystals) compatible with nanoscale features. Like ceramic scaffolds on higher scales, the nanoscaffolds serve as drug carriers for in situ anti-infection and anti-inflammatory purposes, or cell growth carriers for tissue regeneration. Some of the most representative ceramic nanoscaffolds for drug delivery are titania-, CaP- and silica-based (Yang *et al.*, 2010). The mostly used CaP nanoscaffolds usually have structure of CaP cement or silica/CaP nanocomposite. In case of CaP cement nanoporous scaffolds, Xu *et al.* (2008) performed experiments on injectable, nano-apatite, TTCP-DCP-based cement scaffolds, for bone regeneration and delivery of osteogenic cells and growth factors. In addition, Erol-Taygun *et al.* (2019) recently reviewed current knowledge regarding bioglass/polymer nanocomposites, including nanoscale-related features and ion-release effects of bioactive glass with respect to osteogenic and angiogenic responses in vivo and in vitro. The authors also focused on the techniques used to fabricate these nanocomposites.

Although nanocomposites have advantages in enhanced and targeted drug-delivery, there are not enough studies and knowledge about their removal processes from metabolism. Another important issue is toxicity of nanomaterials, as well as their ability to penetrate non-targeted cell membranes. Therefore, the improvement of nanocomposites in DDS has to be continued through further studies in order to better understand and treat numerous diseases.

Conclusions

Bioceramics and bioceramic-based composites have significant impact in controlled and targeted drug delivery and human healthcare. Among various biomaterials, CaP ceramics, CaP cements and bioactive glasses have found the widest application in tissue engineering because of their excellent biocompatibility and biodegradability in physiological environment. As part of DDS, CaPs enable therapeutic efficiency along with limited side-effects. Furthermore, nanocomposites present the added value in DDS offering enhanced and modern therapies with targeted drug delivery in specific medical and pharmacological fields.

Despite the numerous successes of CMC in the research, development and clinical applications, there are lot of addressed challenges that should be achieved, especially at the nanoscale. Nevertheless, this study aimed to present an overview of CaP-based composites in DDS, although the enormous diversity and versatility of CaPs in terms of products and applications cannot be spanned at once. Moreover, their already huge applications are going to be furtherly extended. The previous achievements together with new technological developments will bring ceramic (nano)composites another step further, reaching even broader utilization and clinical applications.

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Advanced Dental Ceramics

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Historical Development of Dental Ceramic

According to the definition, ceramic is an inorganic, non-metallic material that is hardened by a heating process and has approximately 30% crystal structure (Hennicke, 1967). The history of dental ceramics dates back to the period of the ancient pharaohs, when dental crowns and dentures were made of glass or ivory, and were fixed in their places by using gold threads or wires. In 3000 BCE the Egyptians considered dentists as specialist doctors. The Egyptian records described in detail the establishment of medical and surgical procedures that were used in the treatment of dental problems. In China during the reign of the Tang Dynasty (618–907), the porcelain was used for decoration. They were the first to develop a technique of combining appropriate chemical components and baking them at extremely high temperatures. In this way, the production of porcelain dental crowns slowly evolved. European producers tried to produce porcelain on their own, but this topic was kept as a secret for a very long time. However, some of their experiments resulted in the creation of soft porcelain. The first European type of soft porcelain was produced in Florence (Italy) around 1575 (El-Meliegy and van Noort, 2012). The production of porcelain in many parts of Europe began in the 1700s, and competition with Chinese porcelain began. France, Germany, Italy and England had become the largest centers of porcelain production in Europe. In 1717 the French Jesuit pilgrim, Father d'Enrtecolles, was the one who discovered the secrets of the porcelain production craft during a mission to King Te Tching, the largest Chinese porcelain center at that time. This led to the discovery of chemical components, as well as their percentage ratio, which were used by Chinese potters (mineral kaolin 50%, feldspar 25%–30% and silicon dioxide 20%–25%). The use of porcelain in dentistry dates back to 1774, when a French pharmacist named Alexis Duchateau considered replacing his ivory denture with a porcelain denture. He came up with the idea by noticing the great mechanical strength and chemical resistance of his porcelain dishes that he used, and at the same time he was convinced that ivory as a material showed numerous negative characteristics (porosity, liquid absorption, bad breath). So Duchateau and French dentist Nicolas Dubois de Chemant, with the help of a porcelain producer in the factory Guerhard y Saint Germain en Laye, managed to make the first ceramic denture. Subsequently, other materials, such as polymethyl methacrylate, were slowly replaced by porcelain in the production of dental restorations (El-Meliegy and van Noort, 2012; Shen and Kosmač, 2014).

Seventy years later, in 1837, Stockton was the first to make a porcelain tooth. After that, in 1889 porcelain jacket crown was patented and developed by H. Charles, which was further developed and used until the 1950s. The characteristics of dental porcelain were improved by the introduction of the vacuum-firing procedure in 1949. Considering the limitations in terms of strength and durability of porcelain, during the 1950s there were great improvements in the field of porcelain crowns reinforced with a metal base. The combination of both materials, metal and porcelain, had enabled the production of composite materials that are characterized by exceptional mechanical and esthetic properties (metal provides stiffness and strength, while porcelain is in charge of esthetics). These complex systems are known as porcelain fused to metal crowns or metal-ceramic systems (Ubassy, 1993; Powers and Wataha, 2008; Shen and Kosmač, 2014).

Classification

Dentistry has always strived to find new materials, which would replace, by their characteristics, the natural structure of teeth, as accurately as possible. One of the important goals is to minimize the causative wear factors of existing materials, and on that basis to develop the best possible new dental materials (Pantić, 2017). Numerous tribological tests, using appropriate laboratory devices, provide the necessary information from the aspect of verification and confirmation of theoretical conclusions with observed laboratory data (Mitrović *et al.*, 2014; Pantić *et al.*, 2015; Babić *et al.*, 2020). By the development of science in general and the development of dentistry, through various scientific and professional research, the esthetic materials for prosthetic purposes have been developed almost to the extent that their properties meet all required requirements, in the form of esthetics, function and biocompatibility (Pantić, 2017; Pantić *et al.*, 2018b). The excellent characteristics have enabled the wide application of ceramics as a restorative material in the field of esthetic dentistry. Ceramic materials have three main applications (Garber and Goldstein, 1994; Van Noort, 2007), Fig. 1:

- (1) Metal-ceramic crowns/bridges.
- (2) All-ceramic crowns/bridges and veneers.
- (3) Ceramic dentures.

Metal-ceramic systems consist of a metal base, a certain type of metal, and ceramics that are applied over it and give the final look to the crown. The metal base provides stiffness and strength of the system, while the veneering ceramics provide complete esthetics. Alloys containing a high percentage of precious metals (gold-based alloys) or base alloys (cobalt-chromium,

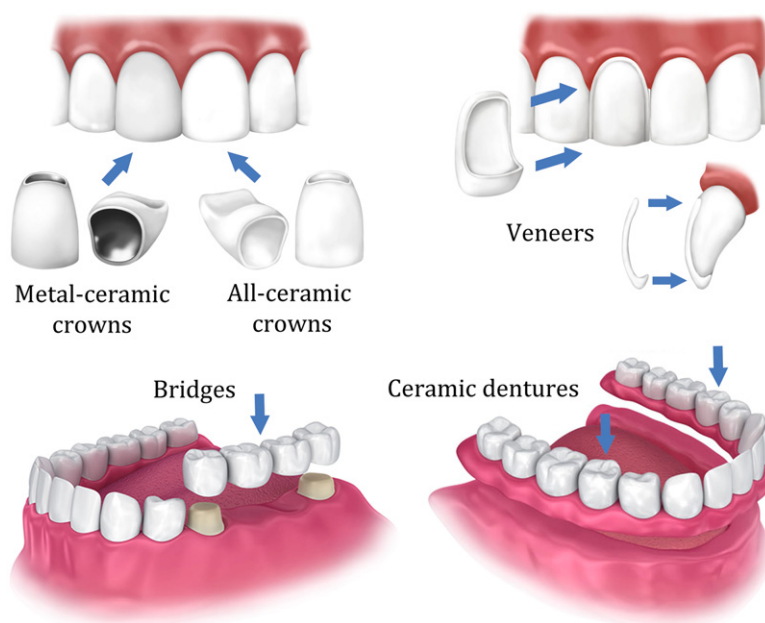


Fig. 1 Different applications of ceramic materials.

nickel-chromium, aluminum-palladium, etc.) are used as the basis for the production of metal-ceramic crowns. However, the opacity feature makes these systems look quite unnatural compared to all-ceramic restorations. In addition, the presence of metals can cause allergic reactions (Touati *et al.*, 1999; Powers and Sakaguchi, 2006; Vallittu, 2013). The clinical disadvantage of metal-ceramic systems is reflected in the fact that it is necessary to remove most of the dental substance (tissue) of a few millimeters, in order to increase the thickness of the restoration. While on the other hand, restorations of new all-ceramic e.g., based on zirconium oxide require the removal of dental substance in an amount of only 0.3–0.5 mm (Pantić, 2017).

The most common causes of failure of metal-ceramic and all-ceramic restorations are related to the delamination problem of veneering ceramics with its base and the formation of cracks in the porcelain base. Considering this, a special attention is paid to the adhesion of dental restorations and dental tissue. The field of dental ceramics is less and less focused on the use of base and precious metals due to the possible presence of allergens, such as beryllium (Be) and nickel (Ni). It can be said that the use of all-ceramic systems is growing day by day, both due to its rapid production by CAD/CAM technology (Computer-Aided Design/Computer-Aided Manufacture) and due to its excellent esthetic and physical-mechanical properties, Fig. 2 (Ho and Matinlinna, 2011).

Ceramics used in esthetic dentistry can be divided into several categories depending on the heating temperature (sintering or crystallization temperature). According to the temperature, ceramic materials are divided into:

- (1) Low-temperature ones, 870–1065°C,
- (2) Medium-temperature ones, 1090–1260°C,
- (3) High-temperature ones, 1315–1370°C.

Low-temperature ceramics are used to make metal-ceramic systems, medium-temperature ceramics are used to make ceramic crowns, while high-temperature ceramic materials are used for dentures. High-temperature ceramics are characterized by high hardness and wear resistance, so they are mainly used for the production of dentures (Touati *et al.*, 1999; Powers and Sakaguchi, 2006).

Traditional ceramic materials are based on feldspar, which consists of mineral feldspar (KAlSi_3O_8), quartz (SiO_2), or kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and it is baked at a temperature of 870°C. The most important characteristics of feldspar ceramics are chemical resistance, (abrasion) and biocompatibility (does not cause any irritation and allergic reactions in contact with tissues) (Hämmerle *et al.*, 2008; Ho and Matinlinna, 2011; Lung and Matinlinna, 2012). Since opaque metal components can negatively affect the transparency and esthetics of dental restorations, current trends in esthetic dentistry tend to constant development of ceramic systems that will fully meet all necessary requirements, in the form of high esthetics, function and biocompatibility (Pantić *et al.*, 2018b). In order to ensure the best possible mechanical and optical characteristics of al-ceramic systems, new types of materials with a high content of crystals of aluminum trioxide (Al_2O_3) and zirconium dioxide (ZrO_2) have been developed (Touati *et al.*, 1999).

All-ceramic systems used in esthetic dentistry are composed of a wide range of crystalline phases (~99 vol%). All-ceramic restorations are characterized by exceptional esthetic properties, with a high degree of fragility in the oral environment. The esthetic appearance and biomechanical properties of the material largely depend on the distribution and size of the particles, as well as the concentration of the crystals present in the base itself. All-ceramic restorations can be produced using different methods (Schmalz and Arenholt-Bindslev, 2009; Kaminski and Easton, 2009):



Fig. 2 CAD/CAM technology.

Table 1 Types of ceramic systems

<i>Types of ceramics</i>	<i>Their name and chemical composition</i>	<i>Flexural strength</i>
Feldspar	Veenering ceramics (KAlSi_3O_8)	90–110 MPa
Glass ceramics	Fluoroapatite ($\text{SiO}_2\text{-Li}_2\text{O-Na}_2\text{O-K}_2\text{O-ZnO-Al}_2\text{O}_3$)	90–110 MPa
	Leucite ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$)	110–160 MPa
	Lithium disilicate $\text{Li}_x(\text{SiO}_2)_y$	350–400 MPa
Oxide ceramics	Aluminum trioxide (Al_2O_3) _x	600–800 MPa
	Zirconium dioxide (ZrO_2) _x	900–1200 MPa

- Sintering,
- Hot pressing,
- Infiltration technique (slip-casting),
- Machine CAD/CAM processing.

Ceramic restorations are much more complex prosthetic structures that completely replace the external structure of the tooth. The restorations can be made on a metal base, a high-strength ceramic base and it can be made entirely of esthetic ceramic materials. In the second case, where the strength and stiffness of the base become an important precondition for the success of the restoration, especially in the case of lateral teeth that are under a higher degree of load, glass ceramics based on lithium disilicate are mainly used. For much more extensive restorations such as bridges, depending on the load zone, it is possible to use oxide ceramics in combination with glass ceramics. Accordingly, dental ceramics follow a wide range of ceramic systems (El-Meliegy and van Noort, 2012).

Nowadays, there are several different types of ceramic systems in dentistry that meet the high esthetic standards of patients. For easier perception, it is possible to make a division according to their chemical composition and certain physical-mechanical properties (value of flexural strength), as shown in Table 1 (Pantić, 2017).

Feldspar is classic dental material (porcelain) and belong to traditional ceramic materials that have been used in dentistry for many years, while “all-ceramic” include glass ceramics and oxide ceramics. Their detailed description is given further in this paper, as well as the description of the mentioned all-ceramic materials (Pantić, 2017).

Glass Ceramics

In the last few years, glass ceramics has become very important as one of the most frequently used materials in prosthetics, solely due to its excellent esthetic characteristics, good mechanical strength and longevity of restorations. There are many different types of glass ceramics, and depending on their chemical, mechanical and optical characteristics, these ceramics can be used in the form of: inlays, onlays, dental crowns (Fig. 3), veneers and bridges attached to natural teeth or embedded dental posts. In addition to



Fig. 3 Different dental restorations: Inlay, Onlay and Crown.

their excellent biocompatibility, glass-ceramic-based materials always tend to have the same characteristics of natural tooth in terms of esthetics, mechanical strength, wear, and chemical durability in the oral environment (Shen and Kosmač, 2014).

Glass ceramics can be classified, e.g., according to their chemical composition, or according to their field of application. Beall (Beall, 1992) classified silicate-based ceramic glass into three groups based on the main crystallizing mineral phase:

- (1) Silicates such as lithium metasilicate, lithium disilicate, enstatite - MgSiO_3 , diopside - $\text{CaMgSi}_2\text{O}_6$ and wolastonite - CaSiO_3 .
- (2) Aluminum silicates with main phases such as cordierite, beta-quartz, beta-spodumene, beta-eucryptite and anorthite.
- (3) Fluorosilicates, comprising mica glass ceramics with fluorine content, such as fluorophlogopite - $\text{K,Na Mg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$, tetra silicic mica - $\text{KMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$, canasite and fluororichterite.

The gradual expansion of technologies in the glass ceramics production has led to new uses in numerous stages of production of various industrial products. The most famous glass ceramics with the widest application are those based on the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system and which have a high resistance to thermal shock due to their low thermal expansion. They are used e.g., for hobs, oven doors or telescopic mirrors (Bach, 1995). Also, glass ceramic is an ideal material for the design and production of bioceramics, which is characterized by exceptional mechanical properties. It is very important to consider the contribution of the dominant arrangement of the mineral phase in bioceramics. Glass ceramic based on the formation of the apatite crystalline phase is very close in chemical composition to human bones, but the use of these materials in orthopaedics is limited due to the lack of mechanical strength and durability of the material (El-Meliegy and van Noort, 2012).

In esthetic dentistry, the first real breakthrough in the development of glass ceramics was made by the company Ivoclar Vivadent with its IPS Empress system, in 1991. It is a leucite glass ceramic whose resistance, optical quality, as well as new hot-pressing material shaping technology have paved the way to success (ISO 23146, 2008). Further development of glass ceramics was achieved in 1998 with the advent of the IPS Empress 2 systems based on lithium disilicate (ASTM C1161, 2002). The material is characterized by a high value of flexural strength and wide application in the productions of restorations and bridges. To achieve an additional esthetic effect, IPS Eris for E2 was developed where fluoroapatite crystals represented the main part responsible for the optical characteristics of the material. The constant presence and use of PRESS and CAD/CAM technologies in all-ceramic materials has led to the development of a new advanced all-ceramic systems called IPS e.max (Ivoclar Vivadent). The materials are intended for PRESS and CAD/CAM technology and possess excellent esthetic and physical-mechanical properties. The IPS e.max system covers a wide range of indications of all-ceramic restorations in different load zones, combining high flexural strength, esthetics and ease of manufacture. Even better results have been achieved in the form of a higher value of the material flexural strength, with the development of new oxide ceramics based on zirconium. The flexural strength of Y-TZP (Yttrium-stabilized Tetragonal Zirconia Polycrystal) is very similar to metals, so it is already used as a complete replacement for metal ceramic systems. In the last few years, CAD/CAM technologies have become increasingly important and without them it is completely unimaginable to make all-ceramic esthetic restorations (Ivoclar-Vivadent, 2005; Ritzberger et al., 2016).

Leucite – IPS Empress CAD

Commercial material IPS Empress CAD (Ivoclar Vivadent, Lichtenstein) is a glass ceramic based on leucite phase system $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$ intended for CAD/CAM technology. The blocks were cast in one piece and were in the semi-crystallized phase. The raw material enables fast processing on the CAD/CAM system into the desired form, where after crystallization the final form of leucite restoration (flexural strength of 160 MPa) is obtained, Fig. 4. IPS Empress CAD has an excellent esthetic appearance thanks to the high and adjustable translucency of the material itself, due to the fact that crystals and glass have a similar refractive index. They also have the possibility of coloring glass in shades that completely correspond to the natural tooth, by adding metal oxide pigments. Although the flexural strength of leucite glass ceramic is 120–150 MPa, as opposed 90 MPa of conventional porcelain, it is still insufficient for fixed bridges in high load zones. Their application mainly includes veneer zones, inlays and onlays as well as anterior single-member restoration (crown) (Shen and Kosmač, 2014).

The microstructure of IPS Empress CAD consists of a glass matrix of leucite crystals (KAlSi_2O_6) which make up 35–45 vol%, while chemical composition is of the following content: ~63 wt% SiO_2 , ~18 wt% Al_2O_3 , ~12 wt% K_2O , ~5 wt% Na_2O , other oxides 0.5–7 wt% and pigments 0.2–1 wt%. The crystals are tetragonal in shape, 1–5 μm in size, and are evenly and densely



Fig. 4 Leucite IPS Empress CAD blocks, raw material and final restorations processed by CAD/CAM technology.

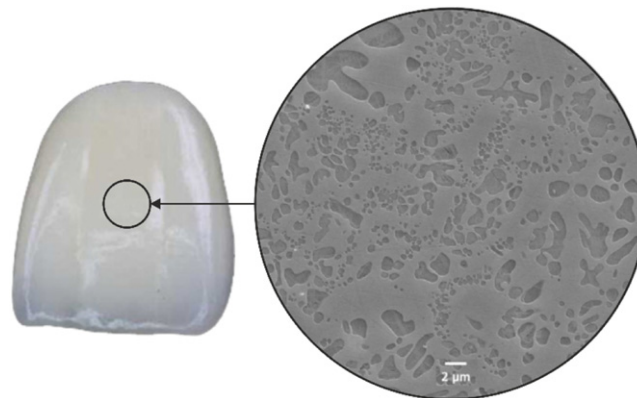


Fig. 5 SEM microstructure of polished IPS Empress CAD, etched in 40% hydrofluoric acid for 20 s.

distributed in the glass matrix itself (**Fig. 5**). The distribution and size of leucite crystals greatly influence the mechanical and esthetic characteristics of the restoration itself. The amount of crystals and the crystallization kinetics were determined by thermal treatment and chemical composition of the treated glass (Bühler-Zemp *et al.*, 2011; Shen and Kosmač, 2014).

By adding components such as Na_2O , Li_2O (1–3 wt%) to the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, in the form of nucleating agents, the temperature fusion of the glass is reduced and the crystallization process itself is accelerated. The final microstructure of crystallized leucite fully corresponds to its physical-mechanical properties, which are presented in **Table 2** (Bühler-Zemp *et al.*, 2011). A large number of tetragonal crystals, densely distributed in the glass matrix, form a crystal structure and their distribution greatly complicates the formation of cracks and their eventual spread.

Leucite (IPS Empress CAD) are available in different colors and shades of translucency, as well as in the form of multi-blocks as the most represented product of the IPS Empress CAD palletes. Due to their completely natural color and fluorescence, as well as the gradual transition between the dentinal and occlusal area, they give maximum esthetics and a completely natural look to the restorations, without additional characterizations. For smaller restorations, e.g., inlays, high translucency blocks are mainly used due to their natural (chameleon) appearance, while the lower translucency blocks are ideal for bigger restorations, e.g., partial or complete individual restorations (bridges).

Lithium Disilicate – IPS e.max CAD

Commercial material IPS e.max CAD is lithium disilicate glass ceramic, intended for CAD/CAM and systems with pressing technology. The blocks for CAD/CAM are blue, cast in one piece and are in the metasilicate phase (partially crystallized, Li_2SiO_3), **Fig. 6**. As a raw

Table 2 Physical-mechanical properties of commercial material IPS Empress CAD

Physical-mechanical properties	Crystallized material
Flexural strength (biaxial)	160 MPa
Fracture toughness	1.3 MPa m ^{1/2}
Vickers hardness (HV)	6200 MPa
Young's modulus	62 GPa
Coefficient of thermal expansion	17.5 × 10 ⁻⁶ K ⁻¹
Density	25 ± 0.1 g/cm ³
Chemical solubility	25 µg/cm ²
Opacity	0.4–0.7
Transformation temperature	625 ± 20°C

Note: Fischer, K., Bühler-Zemp, P., Völkel, T., 2011. Scientific Documentation IPS e.max CAD. Schaan: Ivoclar-Vivadent AG.



Fig. 6 Lithium disilicate IPS e.max CAD blocks, raw material and final restorations processed by CAD/CAM technology.

material, their flexural strength value is low, which allows them to process quickly on a CAD/CAM system. After the crystallization process, the blocks obtain the final crystalline form of $\text{Li}_2\text{Si}_2\text{O}_5$ which is characterized by a high value of flexural strength (~ 360 MPa). IPS e.max CAD is a type of all-ceramic that is characterized by high esthetic quality, so it can be said that its characteristics meet all prosthetic requirements in terms of: esthetics, function and biocompatibility of materials (Pantić *et al.*, 2018b).

SiO_2 and Li_2O are components that form $\text{Li}_2\text{Si}_2\text{O}_5$ crystals, while P_2O_5 is added as a nucleating agent. Other oxides with their characteristics additionally contribute to the structure of the material itself. The chemical composition of IPS e.max CAD is of the following content: 57–80 wt% SiO_2 , 11–19 wt% Li_2O , 0–13 wt% K_2O , 0–11 wt% P_2O_5 , 0–8 wt% ZrO_2 , 0–8 wt% ZnO , 0–5 wt% Al_2O_3 , 0–5 wt% MgO (Fischer *et al.*, 2011).

The glass matrix consists of needle-shaped crystals 1.5 µm long that are randomly oriented and evenly distributed in the glass matrix, Fig. 7 (Höland and Beall, 2002; Höland *et al.*, 2007; Schweiger *et al.*, 2008; Shen and Kosmač, 2014). The physical-mechanical properties of glass ceramics are closely related to its microstructure. A small number of isolated needle-shaped crystals, intertwined in a glass matrix, represent possible fracture zones. The wear of the material takes place tangentially in relation to the force acting on it. Uncontrolled crack propagation is prevented by a large number of needle-shaped intertwined crystals of high strength (Grossmann, 1983). Such a surface structure of the material is characterized by high resistance to fracture (Völkel, 2006; Pantić *et al.*, 2018b).

The material has a clear advantage in translucency over other related materials of this type and in combination with the physical-mechanical properties (Table 3) (Fischer *et al.*, 2011), it possesses, it can be used in high load restoration zones. There are three different sizes of lithium disilicate blocks depending on the type of restoration being performed. IPS e.max CAD can be used as inlays and onlays (minimum thickness 1 mm), veneers (0.4 mm thick), partial or complete restorations (wall thickness of 1.5 mm), as well as bridges of three members.

CAD/CAM blocks are available in different colors (5–16 A-D Vita shades and 4 shades of white) and four levels of translucency, which are controlled by crystal nanostructure (high translucency - HT, medium translucency - MT, low translucency - LT and high opacity - HO). Coloration is achieved by adding certain metal oxides directly to the crude powder which is later dissolved in the glass matrix. Such metal ions are V^{3+} (yellow), Ce^{4+} (yellow) and Mn^{3+} (brown). The restoration can be further modified with additional colors and glaze, or coated with special veneering ceramics (IPS e.max Ceram) using the veneering technique. Glazing is performed as a form of finishing in order to eliminate the surface porosity of the material that can cause the accumulation of

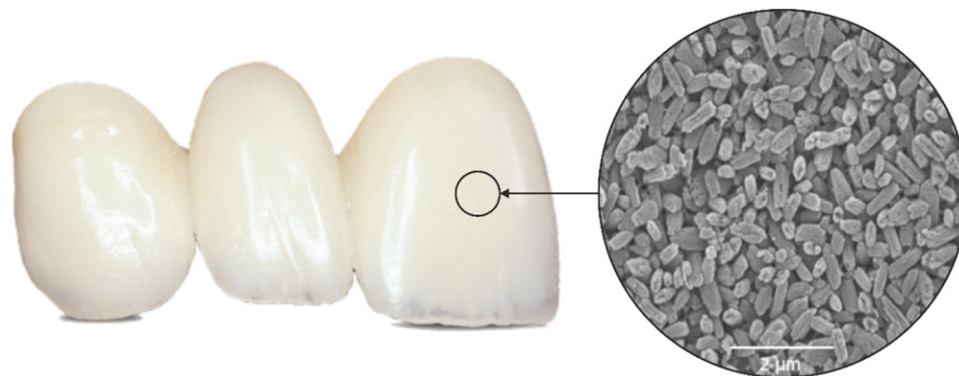


Fig. 7 SEM microstructure of IPS e.max CAD, etched in hydrofluoric acid for 30 s.

Table 3 Physical-mechanical properties of commercial material IPS e.max CAD

<i>Physical-mechanical properties</i>	<i>Fully crystallized state</i>
Flexural strength (biaxial)	360 ± 60 MPa
Fracture toughness	$2\text{--}2.5$ MPa m ^{1/2}
Vickers hardness (<i>HV</i>)	5800 ± 200 MPa
Young's modulus	95 ± 5 GPa
Coefficient of thermal expansion	$10.45 \pm 0.4 \cdot 10^{-6}$ K ⁻¹
Density	25 ± 0.1 g/cm ³
Chemical solubility	$30\text{--}50$ μg/cm ²

Note: Fischer, K., Bühler-Zemp, P., Völkel, T., 2011. Scientific Documentation IPS e.max CAD. Schaan:Ivoclar-Vivadent AG.

bacteria and their further spread. Glazing, as a finishing processing, makes the surface less porous, shinier, additionally reinforced and impermeable to the base material (Völkel, 2006; Fischer *et al.*, 2011; Raghavan, 2012).

Veneering Ceramic – IPS e.max Ceram

IPS e.max Ceram is a nano-fluoroapatite glass ceramic available in powder form with a low melting point. The purpose of this ceramic is mainly for veneering and characterization of various all-ceramic restorations, whether they are made by PRESS or CAD/CAM technology, based on lithium disilicate and zirconium oxide. During the development of veneering ceramic IPS e.max Ceram, the main emphasis was on esthetics and various applications on the mentioned all-ceramic systems. In terms of esthetics, excellent results have been achieved using nanoparticles of fluoroapatite in glass ceramics, as a translucency agent, whose structure is similar to natural teeth (Fig. 8). The refractive index of the crystal is between 1.63 and 1.67 (Pantić *et al.*, 2018a).

The only natural ingredient used in the production of silicate glass is quartz sand. Veneering ceramic consist of a multi-component system SiO₂-Li₂O-Na₂O-K₂O-ZnO-Al₂O₃. The glass structure of fluoroapatite is additionally strengthened by a certain wt% of components CaO, P₂O₅ and F. These three basic components are a prerequisite for the formation of the fluoroapatite crystal Ca₅(PO₄)₃F. Thus, the formed content of fluoroapatite has a great influence on the natural esthetic appearance of the restoration itself in the form of reflection, translucency and opalescence. The main component of the system is SiO₂ with a ~62 wt%, The chemical composition of commercial veneering ceramic IPS e.max Ceram is: 60–65 wt% SiO₂, 8–12 wt% Al₂O₃, 6–9 wt% Na₂O, 6–8 wt% K₂O, 1–3 wt% CaO, 2–3 wt% ZnO, 1–2 wt% Li₂O, 1–1.5 wt% ZrO₂, 1–2 wt% F, + other oxides: SrO, B₂O₃, TiO₂, P₂O₅ (Völkel, 2006; Shen and Kosmač, 2014). Oxides of Al₂O₃ and ZrO₂ in the matrix itself improve the chemical resistance, temperature stability and mechanical strength of the ceramic material. The presence of oxide alkali metals K₂O and Na₂O is very important for optimizing the coefficient of thermal expansion and processing temperature. Depending on the content of mass fraction of SiO₂ and Al₂O₃, the amount of alkali metal oxides varies proportionally in the structure of the material (Völkel, 2006; Pantić *et al.*, 2018a).

Veneering ceramic IPS e.max Ceram is, as previously mentioned, a homogeneous mixture of fluoroapatite glass ceramic and sintered glass particles in the form of powder. Fig. 9 shows the SEM analysis of the nanoscale fluoroapatite crystals shape (less than 300 nm in length and approx. 100 nm in diameter) of the IPS e.max Ceram veneering ceramic.

In clinical use, veneering ceramics are exposed to high chemical, thermal and mechanical stress. The initial measured value of flexural strength of the material cannot be considered the actual value, since the preparation techniques and the homogeneity of the material production process significantly affect the obtained values. It is generally known that glass and ceramics are fragile and



Fig. 8 Veneering ceramic IPS e.max Ceram in powder form and veneering restorations of high esthetic appearance.

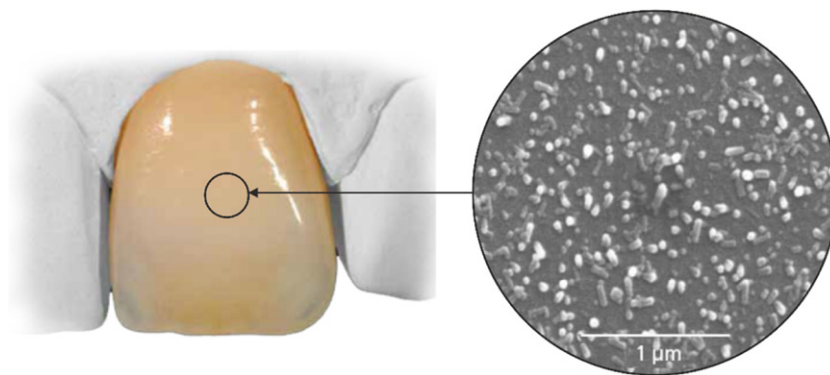


Fig. 9 SEM microstructure of veneering ceramic IPS e.max Ceram.

stiff materials and are not susceptible to plastic deformations until certain surface defects occur, as a result of the elastic behavior of the material itself. In fragile and stiff materials, common fracture points are surface defects of the material in the form of certain surface cavities or porosity of the material itself (Pantić, 2017; Pantić *et al.*, 2018a).

IPS e.max Ceram achieves flexural strength values between 80 and 100 MPa and thus easily meets the requirement of the standard (ISO 6872) which is > 50 MPa. Fluoroapatite crystals do not strengthen glass ceramics, while leucite and lithium silicate crystals strengthen it. The deposition density is too low and the difference in the coefficient of thermal expansion compared to the glass matrix is considerably small in order to strengthen the dispersion. Due to the high content of glass in the matrix of the material, ceramic veneers represent the weakest part of ceramic restorations. Therefore, one must always strive to make the most of the framework dimensions. This is particularly refers to the area of heavy loads (posterior area). The design of the crown itself can improve the mechanical reliability of the restoration itself. Table 4 shows the physical-mechanical properties of commercial veneering ceramic IPS e.max Ceram (Bühler-Zemp and Völkel, 2005b).

Zirconium Dioxide

Zirconium has been known as a term since ancient times. Jacinth, a red gemstone made of zircon, was mentioned in the “Apocalypse of St. John” as one of the stones that were part of the walls of St. Jerusalem. The name zircon is derived from the old Persian word “zar gun”, which means the color of gold. In 1789, the German chemist Martin Heinrich Klaproth discovered zirconium dioxide (ZrO_2), after he isolated it by heat treatment from a precious stone jacinth, which was brought to him from the Middle East. Thanks to its exceptional properties, he called it a “miracle mineral” (Shen and Kosmač, 2014).

Zirconium dioxide (ZrO_2) is a chemical compound of Zr^{4+} metal ions and O^{2-} oxygen anions. The result is an oxide compound of ionic character, which despite the Zr^{4+} metal ion does not belong to metals but to a group of non-metallic inorganic compounds. It is basically wrong to speak of metal in this context, for the reason that it is obvious that zirconium oxide ceramics are composed of a fine, granular, polycrystalline structure (Völkel, 2006). Zirconium dioxide has been used for more than 20 years as a material that with its excellent characteristics meets all high standards in various fields of industry and medicine. The reason

Table 4 Physical-mechanical properties of commercial material IPS e.max Ceram

<i>Physical-mechanical properties</i>	<i>Sintered material</i>
Flexural strength (biaxial)	90 ± 10 MPa
Vickers hardness (<i>HV</i>)	5400 ± 200 MPa
Firing temperature	750/760°C
Coefficient of thermal expansion	9.5 ± 0.25 10 ⁻⁶ K ⁻¹
Chemical solubility	15 ± 5 µg/cm ²
Glass transition point <i>T_g</i>	490 ± 10°C
Amount of fluorapatite in the glass ceramic	19–23 wt%

Note: Bühler-Zemp, P., Völkel, T., 2005b. Scientific Documentation IPS e.max Ceram. Schaan: Ivoclar-Vivadent AG.

for that is the excellent crystal-chemical, as well as physical-mechanical characteristics of ZrO₂. Based on these characteristics, Garvie described zirconium dioxide as a “ceramic steel” (Garvie *et al.*, 1975).

In the last few decades, zirconium has been widely used as a substitute for metal in various fields. The first breakthrough in the clinical use of Y-TZP ceramics was introduced by the French company Ceramiques Techniques Desmarquest (St. Gobain) in 1990. Thanks to the work of the team, led by Calés and Christel (Christel *et al.*, 1989), Y-TZP material was added to the list of high-performance bioceramic materials. It was mainly used for the production of certain parts of the artificial hip, which also represented the first application of zirconium as a biomaterial in medicine. Namely, its high values of flexural strength, compressive strength and modulus of elasticity have led to the fact that it can absolutely match the mechanical characteristics of the metal. In addition, zirconium is biocompatible, which means that it does not cause any irritation or allergic reactions in contact with tissues, which allows its use in medicine (artificial hips, hearing aids, etc.) and in dentistry (Pantić, 2017).

The first use of zirconium in dentistry was present in the production of dental posts, fixed dentures and dental implants, and very often in the literature the term “white steel” could be found (Garvie *et al.*, 1975; Sandhaus and Pasche, 1994). However, the real breakthrough of materials in esthetic dentistry came with the development of CAD/CAM technology (Piconi, 2008). The use of zirconium in combination with CAD/CAM computer systems is now expanding and developing both due to the excellent characteristics of new zirconium materials and due to the precision and speed of production brought by the new production technology. This way of making restorations enables perfect adhesion of crowns and bridges to the gingiva, thus providing patients with excellent quality, comfort and longevity of restorations, in all load zones. However, it should be noted that in terms of its hydrothermal durability, the material to a certain extent has weaker properties than metals (Sato and Shimada, 1985; Lange *et al.*, 1986).

Various studies have shown that pure Y-TZP is more susceptible to t→m transformation during the material aging at a temperature range of 70–250°C, in a humid environment. The result is a loss of mechanical strength. One type of corrosion occurs, which is similar to the one which occurs with metals. Consequently, ZrO₂ also has metallic properties in this respect. By adding additional agents, such as Al₂O₃ and CeO₂ in small amounts, these negative properties of Y-TZP are significantly improved to such an extent that they become almost negligible (Sato *et al.*, 1986). The IPS e.max ZirCAD material contains about 0.25% Al₂O₃ which improves the behavior during aging in such a way that there is no risk of loss of mechanical strength due to a hydrothermal exposure.

Zirconium – IPS e.max ZirCAD

IPS e.max ZirCAD is a presynthesized Yttrium-stabilized Tetragonal Zirconia Polycrystal (Y-TZP) in the form of a block containing small amounts of yttrium oxide intended for processing by CAD/CAM technology (Fig. 10).

There are different block sizes of IPS e.max ZirCAD depending on the load zone and the type of restoration being performed. The block is white, chalky in structure and in the preinterrupted state it is characterized by porous morphology (50%). The hardness value of the raw material is very low, which allows quick and easy processing of the block on the CAD/CAM system in the desired shape. After molding, the material is heat-treated (sintered) in a high-temperature furnace specially developed for oxide ceramics at a temperature of 1500°C. During the sintering process, which lasts 8 h, the crystals form a final tetragonal homogeneous structure and obtain their final flexural strength in the value of over 900 MPa (Fig. 11) (Bühler-Zemp and Völkel, 2005a; Pantić, 2017; Pantić *et al.*, 2019).

What is very important during the sintering process is that the cooling and heating gradients are coordinated with the parameters of the sintering procedure. During the sintering process, the volume of the material decreases proportionally (shrinks) by ~20% compared to the original size. This volume reduction has already been taken into account during the making of restoration by CAD/CAM technology. The chemical composition of IPS e.max ZirCAD is of the following content: 87–95 wt% ZrO₂, 4–6 wt% Y₂O₃, 1–5 wt% HfO₂ and 0.1–1 wt% Al₂O₃ (Bühler-Zemp and Völkel, 2005a; Völkel, 2006).

The thermal process of material processing is crucial for the formation of the microstructure. If the heating process is not precisely controlled, the result will be a number of undesirable results that often cannot be seen visually. During the sintering process, the color of the material changes visibly and the restoration acquires a slight transparency in relation to the raw material.

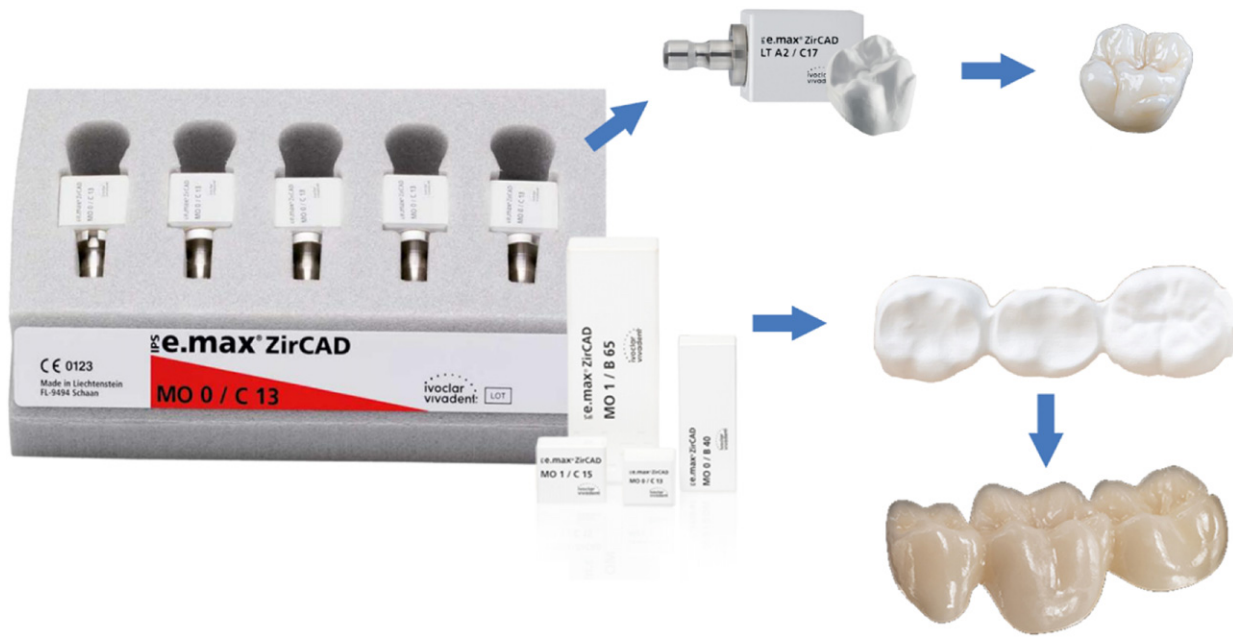


Fig. 10 IPS e.max ZirCAD blocks, raw material and final restorations processed by CAD/CAM technology.

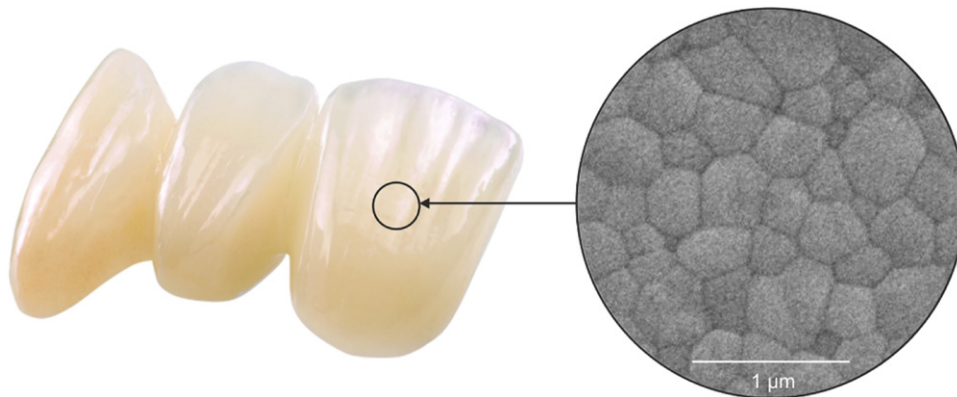


Fig. 11 SEM microstructure of sintered IPS e.max ZirCAD.

After sintering, the porosity of the material was reduced to a minimum. Sintered tetragonal crystals forming a homogeneous structure of IPS e.max ZirCAD material can be clearly seen in the completely condensed structure (**Fig. 11**). Therefore, the number of errors in the structure is also reduced to a minimum. The combination of high density, low error rate in the structure and small crystal size ($0.5\ \mu\text{m}$) results in a high value of flexural strength of the material. The flexural strength of Y-ZTP (900 MPa) is superior compared to other dental ceramics and is far higher than the yield strength of metallic alloys used in dentistry. Other physical-mechanical properties of the sintered material are shown in **Table 5** (Bühler-Zemp and Völkel, 2005a).

Thanks to its high mechanical strength, the material is suitable for use in almost all indications that have so far been reserved exclusively for prosthetic restorations reinforced with a metal base. IPS e.max ZirCAD is mainly used to make the dental base which is further veneered with IPS e.max Ceram ceramics, in order to achieve the appropriate natural esthetic appearance of the restoration (Pantić, 2017).

Conclusion

The revolution in the development of esthetic materials, new technologies and high-tech equipment in dentistry is conditioned by both the requirements of patients and the growing competition among leading companies and producers of dental materials and equipment. Nowadays, restorative dentistry strives for the constant improvement of old and the development of new esthetic

Table 5 Physical-mechanical properties of commercial material IPS e.max ZirCAD

<i>Physical-mechanical properties</i>	<i>Sintered material</i>
Coefficient of thermal expansion	$10.75 \pm 0.25 \cdot 10^{-6} \text{K}^{-1}$
Flexural strength (biaxial)	$900 \pm 50 \text{ MPa}$
Vickers hardness (<i>HV</i>)	13,050 MPa
Fracture toughness	$5.5 \pm 0.22 \text{ MPa m}^{1/2}$
Density	6.045–6.065 g/cm ³ (99.4%–99.7%)
Medium size of crystallites	$0.52 \pm 0.05 \mu\text{m}$
Chemical solubility	1 $\mu\text{g/cm}^2$

Note: Bühler-Zemp, P., Völkel, T., 2005a. Scientific Documentation IPS e.max ZirCAD. Schaan: Ivoclar-Vivadent AG.

materials that will enable the complete replacement of the natural structure of the teeth and thus satisfy the needs of all patients. From year to year, the standards and criteria of what is considered a beautiful and creative imitation of a natural tooth are growing. Therefore, the main goal of esthetic dentistry is based on the natural appearance of the prosthetics itself.

One of such advanced materials in restorative dentistry is all-ceramics, which is the highlight of today's esthetic dentistry. By combining all-ceramics and CAD/CAM technology, perfect prosthetic works are obtained in the form of various dental restorations. CAD/CAM technology is the most modern computer-aided process for processing finished ceramic blocks, by the machine milling. In this way, the precision and speed of production have been significantly improved, as well as the appearance of esthetic restorations in relation to the previous classic technology of making dental restorations, which was performed manually.

Until recently, in dentistry, in terms of esthetics, metal-ceramics were the best possible replacement for a natural tooth. Today, modern esthetic dentistry cannot be imagined without the use of all-ceramic materials, because their natural appearance meets the expectations of even the most demanding patients in every respect. Numerous studies have shown that all-ceramics do not cause any harmful effects on the human health. The characteristics of these materials are durability, high strength, complete biocompatibility, not causing any allergic reactions, complete all-ceramics construction, natural appearance and excellent esthetics.

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Further Reading

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Smart Composite Materials: An Introduction

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Interest in smart (intelligent or responsive) materials, and of composite materials in particular, has been steadily increasing over the past decade. This is testified by the number of publications and filed patents on the topic. The fact that one or more properties of a multimaterial can be changed in a controlled manner by means of external stimuli is undoubtedly appealing in sensing and actuation fields. Smart composite materials can be engineered (and applied) into different length scales, ranging from large structural components to miniaturized devices as those currently deployed in the area of wearable technology. The articles included in this section aim to grasp the topic of smart composite materials from different viewpoints, namely, synthesis pathways towards smart composites, main sorts of materials combined into a single structure or device, and application fields depending on the stimuli they react to (e.g., temperature, pH, electric field, magnetic field, light, pressure, etc.). In addition, associated challenges and prospects for each type of smart composite material are highlighted.

The article co-authored by Wang and Pham entitled “Smart composites and their applications” offers a glimpse of the area of smart composites. A classification into four major types: (1) sensitive structural composites, (2) composites for actuation, (3) composites with novel functionalities other than sensing and actuation, and (4) nanocomposites is introduced. It is made clear that the understanding of the physical and physicochemical properties of the components involved in a smart composite material, the nature and quality of interfaces between phases, and the accuracy of the fabrication methods are key parameters affecting their correct performance. Key benefits of using smart composites (availability, reliability, and capability to extend design freedom) are overviewed in this article.

In the article entitled “Composite metamaterials: types and synthesis” authored by Schürch and Philippe, newly produced metamaterials characterized by showing exotic mechanical (e.g., auxetic, anepirretic), photonic and phononic, and acoustic properties are overviewed. Many of these fancy materials are produced by additive manufacturing (also known as 3D printing) and lithography. In particular, the manufacturing of composite metamaterials from stereo- and multi-photon lithography and subsequent coating of the resulting polymeric backbone by electroless deposition, atomic layer deposition, chemical and physical vapor deposition is covered. The coating can be a metal, metallic alloy or a semiconductor featuring an imposed architecture.

Further insights into the 3D printing technique are given by Palmero and Bollero. 3D printing has become a very popular fabrication technique due to its ability to create complex, customizable architectures from a 3D computer-aided design (CAD) file. Since its launch by Charles “Chuck” Hull in 1984, continuous improvements in fabrication accuracy, speed, materials (including composites), and costs have been done. 3D printing allows designing devices with regard to efficiency (high performance, materials usage, diminished environmental footprint) instead of availability of components. Indeed, from the various techniques available today for the synthesis of smart materials, we can undoubtedly say that 3D printing is sitting on the throne. In the article coauthored by Palmero and Bollero, a classification and description of additive manufacturing technologies (namely, vat photopolymerization, powder bed fusion, material extrusion, material jetting, binder jetting, sheet lamination and directed energy deposition) is provided. The nature of the components jointly printed to endow the final composite material with reinforcing, magnetic, thermal or electrical capabilities or features is overviewed. The incorporation of active materials into the 3D printing process to make composites whose shape can change over time in response to an external stimulus has opened a whole new paradigm in materials engineering, namely, 4D printing.

The concept of halochromism, a sort of chromotropism, is introduced in the article “Halochromic composite materials” authored by Bilgin. Chromotropic substances are often organic compounds (e.g., anthocyanins) that are sensitive to a variation of a property in the surrounding environment (the pH in the case of halochromic substances) and this is reflected by a change in colour. The latter can be due to, for instance, protonation/deprotonation of the molecule, and can be detected by means of an optical reader, using an image recognition algorithm, or by a simple colour comparison method. Approaches to encapsulate halochromic substances in matrices, shells or even inks open the door to halochromic composites. In this article, the use of halochromic composites in smart sensing like pressure-sensitive sensors, in packaging, or in the control of antifouling and antimicrobial properties of structures exposed to marine environments is tackled. Halochromic substances can also be incorporated in coatings to trigger self-healing processes when some sort of deterioration occurs.

Self-healing (or activation of damage mitigation process) is also of utmost importance in the smart protection of metallic structures. The topic of smart protection of carbon-reinforced composite materials and carbon reinforced polymer (CFRP)-metal joints is covered in the article by Ofoegbu *et al.* These materials are employed in the aeronautical and automobile sectors and are subject to several sources of damage including impacts, static overload, fatigue, creep, hygrothermal effects, galvanic corrosion, overheating and/or lightning strike. Current state-of-the-art of smart protection strategies of these materials, the rationale behind, and the limitations are covered in this article, with an exhaustive analysis of the available literature.

Latest advancements in the field of converse magnetoelectricity using porous composite materials are reviewed by Nicolenco *et al.* in their article “Nanoporous composites with converse magnetoelectric effects for energy-efficient applications”. In particular, ferro- or ferrimagnetic nanoporous solid frameworks filled or coated with another solid phase or a liquid are considered. These materials undergo changes in their magnetic properties (e.g., coercivity, saturation magnetization) under application of voltage and the effects are often exacerbated because of their high surface-to-volume ratio. The mechanisms involved in the magnetoelectric response, which

often act in a simultaneous manner, are put forward. Composite materials in this domain find prospective applications in spintronics, magnetic sensors/actuators and memories.

Magnetic fields are also involved in the so-called magnetocaloric effect materials, which are mostly devised for refrigeration and air conditioning applications as a more efficient alternative to conventional gas compression cycles. Compared to single-phase materials, magnetocaloric composites benefit from the combination of different components or phases to either improve the magnetocaloric effect or add additional functionalities to refrigerator beds (i.e., higher mechanical stability, thermal conductivity, and corrosion resistance, alternative designs, or the possibility to actuate the device with fields other than magnetic ones). In their article, Law and Franco cover the fundamentals of the magnetocaloric effect, and the latest advancements in refrigerator beds design including the stacking of layers (or the packing of microwires) of a given system, e.g., an alloy, for which the chemical composition varies from one layer to the other, multiphase magnetocaloric materials, and magnetocaloric composites with added functionalities besides the magnetocaloric effect. The most convenient figure of merit for magnetocaloric composites is discussed as well as the techniques for prediction and study of magnetocaloric composites and the magnetocaloric effect.

In the article co-authored by Carvalho *et al.*, the definition, properties, types and application of piezoelectric composites, typically made of polymeric matrices (e.g., poly (vinylidene fluoride), nylon-9, polyurea, etc.) and ceramic fillers, are covered. Piezoelectric materials are a class of dielectric materials whose polarization can be varied upon application of mechanical stress and vice versa. Thanks to the addition of fillers, the polymeric composites often show higher piezoelectric coefficient values than pristine polymers. Recent applications in electronics, energy harvesting, environmental sensors and health monitoring are discussed.

The morphing capabilities of adaptive composite materials are covered from both experimental and theoretical standpoints in the articles authored by Fornell and Riccio *et al.*, respectively. The use of modelling tools like the user defined material model (UMAT) subroutine implemented in the Abaqus Standard Finite Element (FE) environment allows simulating and predicting the behavior of shape memory alloys, as demonstrated by Riccio *et al.* The authors show a particular case study of a bi-stable biased actuator operated by shape memory alloy springs. On the other hand, the design, synthesis routes, and applications of magnetic shape memory composites are surveyed by Fornell. A distinction is made between composites for which the magnetic shape memory reinforcement phase is incorporated into a polymeric matrix (e.g., silicone), and those for which the polymeric matrix provides the shape memory functionality and the filler affords ferro- or ferrimagnetic properties (e.g., magnetite nanoparticles). Applications in damping, actuation, and biomedicine are covered. In most cases, magnetic shape memory composites overcome brittleness and production costs associated with single crystalline shape memory materials.

In the article authored by Vera *et al.*, thermoresponsive composites consisting of a polymer matrix able to show changes in phase and solubility in response to temperature are overviewed. As before, the addition of nanofillers to the polymer matrix can ameliorate some of the drawbacks associated to polymers, i.e., low mechanical robustness, thermal degradation, or poor control over drug release. Poly(N-isopropyl acrylamide) is one of the most studied thermoresponsive polymers to which different nanosized fillers like carbon nanotubes, gold nanoparticles, graphene oxide, or iron oxide nanoparticles are added. As it will be shown in this article, thermoresponsive composites find uses in biomedicine, cosmetics, aerospace, automotive, and environmental sectors.

Finally, the interest of the scientific community towards renewable materials has placed cellulosic composites in a privileged position. In the article authored by Torrents-Barrena and Pellicer, recent contributions of smart cellulose composites to shape-memory, wearable technology, and food packaging applications are overviewed. Considering that machine learning is a burgeoning field with many opportunities in materials science, the second part of the article is devoted to recent examples of different machine learning methods applied to cellulose composites for prediction of properties (e.g., mechanical properties like strength and Young's modulus) and improvement of efficiency of processes (e.g., flocculation of a clay mineral using cellulose nanocrystals).

Smart Composites and Their Applications

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Overview

Smart composites are designed materials having one or more properties that can be changed in a controlled fashion by external stimuli. There has been significant growth in research on smart composites over the past 11 years, as shown in Fig. 1.

According to the Web of Science, 'smart composites' emerged in the late 1980s and early 1990s (Society for Experimental Mechanics U.S., 1990; Talat, 1990; Sirkis *et al.*, 1990; Varadan *et al.*, 1990). The term refers to structural materials with embedded electronic and optic sensing components so that the composites can detect structural stress and strain. The word 'smart' relates to the capability of a structure to sense. Over the years, significant advances have been made in structural health monitoring and relevant sensing technologies.

Research in smart composites has seen many other new developments, including shape-memory composites, smart textile composites, and self-healing composites. The range of materials covered by the term 'smart composites' has been expanding and it is difficult to have a clear and unique definition of that term. Table 1 lists recent 5-year reviews addressing key developments in smart composites. Overall, the term now refers to four general groups of materials: (1) sensitive structural composites; (2) composites for actuation; (3) novel functional composites; and (4) nanocomposites that are enablers of novel functions.

Four Major Types of Smart Composites

Sensitive Structural Composites

Sensitive structural composites are materials that have the sensing capability to detect stress, strain, fatigue and damage. Their development has been driven by the need to monitor the health conditions of structures that are difficult to inspect or repair, such as wind turbine blades, underground pipes and long-span bridges. The conventional way to monitor the condition of a structure is to mount sensors onto it, which makes the sensors vulnerable to external environments and damage. Embedding sensors into structural materials offers an integrated design that is more reliable and compact. Due to its sensing capability, the structure can also be named a 'smart structure' (Sirkis *et al.*, 1990) and 'smart composites' (as the structure is made of more than one type of materials, i.e., host materials and sensors).

Several types of sensors have been adopted in the development of sensitive structural composites. Among them, fiber optic sensors have been widely studied and adopted (Di Sante, 2015; Lau, 2014; Murukeshan *et al.*, 2000). Their features include, but are not limited to, immunity to electromagnetic interference, small size, light weight, durability, low cost for mass production and high bandwidth. These features allow large numbers of sensors to operate in the same system and to be integrated within thin materials (Di Sante, 2015). For example, fiber optic sensors embedded in lightweight fiber-reinforced composites (Fig. 2) can be used to monitor the curing of matrix materials in their fabrication, and their in-service conditions (Leng and Asundi, 2003).

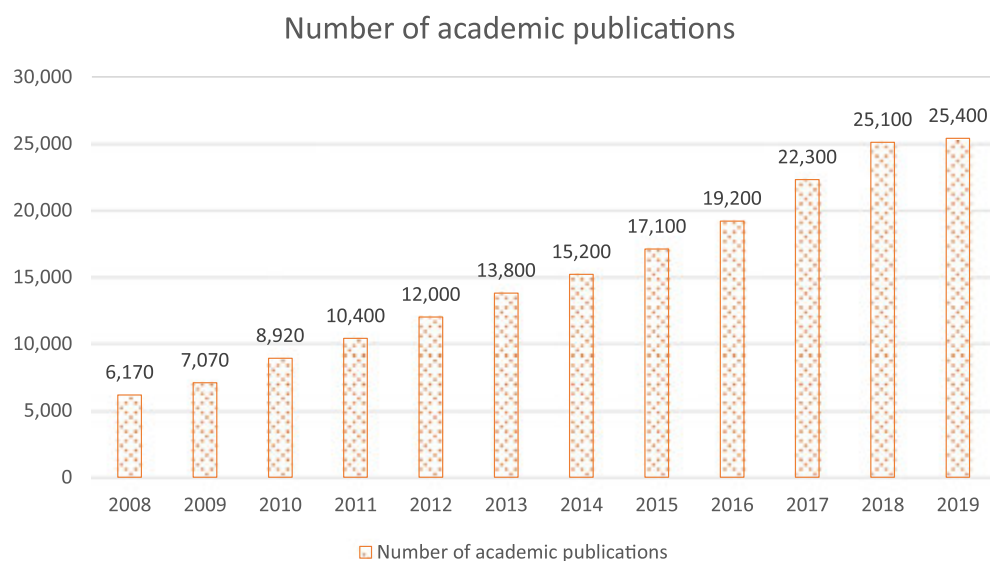


Fig. 1 Number of publications about smart composites based on Google Scholar data.

Table 1 Selected 5-year academic reviews in the field of smart composites

Topics	Time	Key information	References
Electric textiles	2016	- This paper reviews four types of smart electronic textiles: electricity generation, electricity storage, electricity utilization, and their integration. - Fabrication of efficient fibers on a large scale is a challenge. - Connection and weaving of electronic fibers are challenges.	Weng <i>et al.</i> (2016)
3D printing for novel materials	2017	- This paper reviews applications of additive manufacturing to the fabrication of smart composites. 3D printing should be an integral part of a multi-process system rather than a stand-alone operation. 3D printing speed, resolution, and printing materials are considered key to future developments.	Lee <i>et al.</i> (2017)
Graphene-based smart materials	2017	- This paper reviews the effects of graphene on responsive materials (i.e., chemical, electrical, mechanical, thermal, light and magnetic). - Mass production, design of microstructure, biocompatibility and the role of graphene as a smart amount filler can be further investigated/developed.	Yu <i>et al.</i> (2017)
Shape-memory hydrogels	2017	- This paper illustrates structural principles predominately employed in the hydrophobic shape-memory polymers. - Future applications include medicine and soft robotics.	Löwenberg <i>et al.</i> (2017)
Negative Poisson's ratio materials	2018	- This paper reviews the relationships among structures, materials, properties and applications of negative Poisson's ratio materials. - Topology optimization is a powerful tool in future developments.	Ren <i>et al.</i> (2018)
Use of fiber optic sensors in smart aircraft composites	2015	- This paper reviews recent advances and applications of FBG sensors, Brillouin and Rayleigh distributed sensors, to the structural health monitoring of composite aircraft structures. - Improving the reliability, robustness and maintainability is critical to future developments.	Di Sante (2015)
Self-healing composites	2015 and 2016	- These papers focus on composites that can repair themselves following mechanical damage. - There is a lack of suitable computational tools and models to study the healing mechanism in depth.	Patrick <i>et al.</i> (2016), Wang <i>et al.</i> (2015b)
Multifunctional materials	2016	The complexity of fabricating extrinsic self-healing materials is a challenge.	Ferreira <i>et al.</i> (2016)
Shape-memory polymer nanocomposites	2017	- This is an extensive review of major multifunctional materials and their applications. - This paper addresses the stimulus methods for shape-memory polymer nanocomposites. - The importance of dispersion and interface interaction in future developments is highlighted.	Liu <i>et al.</i> (2017)
Smart nanogel composites	2015	- This review focuses on the application of nanogels to nanomedicine. - Pharmacodynamics, metabolism, and pharmacokinetics still need to be assessed before hybrid nanogels are used in practice.	Molina <i>et al.</i> (2015)
Flexible strain sensors	2018	- This paper reviews electrically conductive polymer composites for use as flexible strain sensors. - Performance of flexible strain sensors relies on the conductive fillers' type, structure and loading, and the morphology design of the conductive networks. - New functions additional to sensing (i.e., self-healing and superhydrophobicity) have been introduced to the field.	Liu <i>et al.</i> (2018)

Another popular sensor option is based on piezoelectric materials (Giurgiutiu *et al.*, 2002; Bhalla and Soh, 2004; Park and Inman, 2007; Giurgiutiu, 2005). The piezoelectric effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress. By monitoring and measuring the generated electric charge, it is possible to use piezoelectric materials as sensors. For example, different types of piezoelectric ceramic powders can be incorporated into a cement matrix to enable sensing abilities (Dong and Li, 2005). The laminated piezoelectric architecture embedded inside the cement matrix and the fabricated cement composites are given in Fig. 3. Not only rigid materials, but also less stiff composites such as hydrogel polymers can adopt piezoelectric mechanisms. For example, BaFe₁₂O₁₉ nanoparticle cross-linked PAA hydrogel has a smart and flexible piezoresistive strain sensing capability (Gu *et al.*, 2019).

A unique characteristic of the piezoelectric effect is that its ability to transform stress to electricity is reversible, meaning that the materials can generate stress when an electric field is applied. This allows 'smart composites' to not only *sense* but also *actuate* (Zhang *et al.*, 2002; Pelrine *et al.*, 2000). This bridges *sensitive composites* and another important group of smart composites, *composites for actuation*.

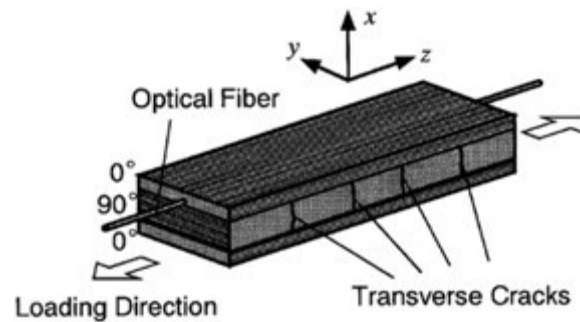


Fig. 2 Embedding a fiber optic sensor in a laminated fiber-reinforced composite. Reproduced from Okabe, Y., Tanaka, N., Takeda, N., 2002. Effect of fiber coating on crack detection in carbon fiber reinforced plastic composites using fiber Bragg grating sensors. *Smart Mater. Struct.* 11 (6), 892–898.

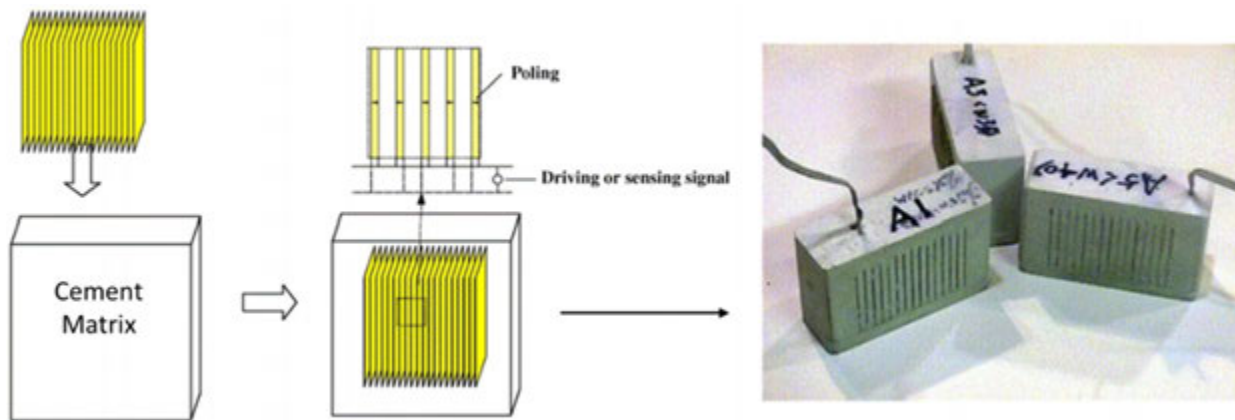


Fig. 3 Smart cement composites incorporating piezoelectric sensing materials. Reproduced from Dong, B., Li, Z., 2005. Cement-based piezoelectric ceramic smart composites. *Compos. Sci. Technol.* 65 (9), 1363–1371. (Special issue).

Composites for Actuation

Materials being used as actuators were referred to as induced strain actuators in the 1980s. The actuation was based on natural mechanisms that cause actuation strains, including thermal expansion, piezoelectricity, electrostriction, magnetostriction, material phase change and moisture absorption (Crawley and Lazarus, 1991).

Shape-memory materials were proposed and developed based on the above mechanisms. They are a group of materials capable of deforming in response to certain stimuli. Since their emergence in the 1980s, this area has continuously grown and is now a major branch of the field of smart composites (Liu *et al.*, 2014).

Shape-memory composites can be manufactured at a low cost; they are also lightweight and potentially biocompatible and biodegradable, facilitating applications such as space-deployable components and structures (e.g., antennas and hinges (Sokolowski *et al.*, 2008, 2004), as shown in Fig. 4) and biomedical artificial muscles (Rodriguez *et al.*, 2012).

Shape-memory composites can be controlled using temperature, electricity, magnetic field and light (Liu *et al.*, 2017), making them flexible in their implementation. After years of development, their recovery stress, production cost and displacement resolution have all been improved significantly (Chen *et al.*, 2018).

Additional to displacement control, another type of composite actuator (which is also based on piezoelectric effects) can be used to control the vibration of a structure. Its mechanism is to take advantage of piezoelectric actuators' tuneable stiffness, so that the energy in vibrations can be absorbed in a controlled way. Using this mechanism requires careful designs and optimizations of the placement of the piezoelectric sensor and actuators (Biglar *et al.*, 2015). A review of the use of piezoceramics in the vibration of civil structures is also available (Song *et al.*, 2006).

Composites with Novel Functionalities

Smart composites can also be composites with unusual properties (additional to sensing and actuation). Here are a few selected examples.

Electromagnetic wave absorbing materials are materials incorporating elements (for example, nanoparticles) with electromagnetic wave absorbing properties. Researchers have recently created wave absorbing Sn/SnO₂@C composites with tunable Sn content, which alters the material's response to the applied bias voltage, giving it tunable frequency-transmission properties (Lv *et al.*, 2019). A recent study

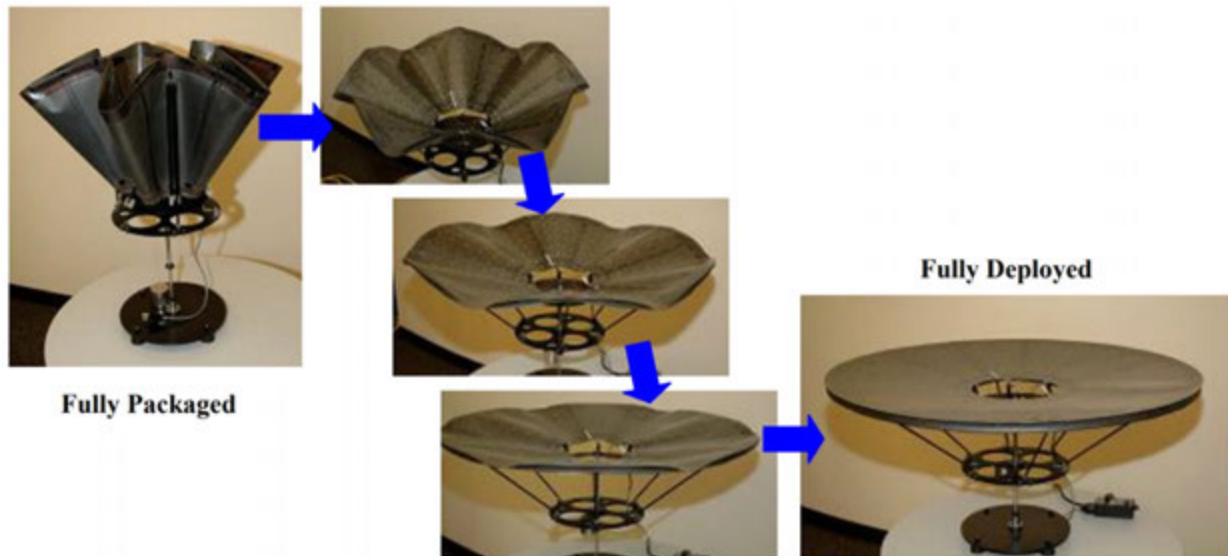


Fig. 4 Deployment of space-use component using shape-memory composites. Reproduced from Keller, P.N., Lake, M.S., Codell, D., *et al.*, 2006. Development of elastic memory composite stiffeners for a flexible precision reflector. In: Collection of Technical Papers – AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference, pp. 6984–6994.

on smart composite absorbers also indicates the possibility of wave absorbing capabilities at gigahertz frequencies (Idris *et al.*, 2016), which is the frequency spectrum essential to radio astronomy, next-generation telecommunications, defense and security.

Self-healing composites are composite materials that can recover automatically after damage (Wang *et al.*, 2015b). The mechanism of healing can be either intrinsic or extrinsic. Intrinsic healing uses materials' intrinsic features (e.g., swelling, melting) (Huynh *et al.*, 2017). Extrinsic healing is based on embedded microstructures (e.g., microcapsules and microvessels) which contain liquid healing agents. In the event of a crack, the healing agents are released to fill the gap and solidify (Pang and Bond, 2005), as shown in Fig. 5. Extrinsic healing can be affected by a number of factors including the pattern of the microstructures (Wu *et al.*, 2011), the type of healing agents, the environmental conditions (Wang *et al.*, 2016). Hence, the development of self-healing materials is a very interdisciplinary research area. The self-healing function can also be incorporated with other functions. For example, dynamic imine bonds based on polyazomethine (PAM) as molecular interconnects and Fe_3O_4 -loaded multiwalled carbon nanotubes can be used to build wave-shielding materials that can self-heal (Dai *et al.*, 2019). Self-healing composites' potential applications are mostly connected with safety-critical machines and infrastructures that may be difficult to access, inspect, maintain and repair, such as off-shore wind turbines, aircrafts and satellites.

Artificial skins with very good stretchability and sensing capability have grown rapidly in the last decade. They are soft and stretchable materials with embedded electronic sensing components. For example, conductive elastomeric composites incorporating carbon nanotubes (Roh *et al.*, 2015) can be stretchable, transparent, ultrasensitive and patchable, making them suitable for use as human-machine interfaces (Roh *et al.*, 2015). Artificial skins can sense touch, temperature, humidity and biological variables (Kim *et al.*, 2015). The color of electronic skins can also be tuned by embedding organic electrochromic devices (Chou *et al.*, 2015). There has also been work on skins with self-powering capability (e.g., through triboelectric mechanisms) (Shi *et al.*, 2016) (Fig. 6).

Stretchable and sensitive fibers are seen as a key enabler of wearable devices and electronics textiles (Weng *et al.*, 2016). A number of approaches have been proposed including using the 'compression spring' structure to build graphene-based composite fibers (Cheng *et al.*, 2015), and incorporating silver nanowires and nano particles in elastomeric fibers (Park *et al.*, 2012; Lee *et al.*, 2015).

Smart membrane composites can be used in the separation of oil and water (Li *et al.*, 2017, 2015). Oligoaniline being added to a vitrimer allows the composite to respond to six different stimuli (heat, light, pH, voltage, metal ions and redox chemicals) and perform six functions (shape memory, welding, healing, recycling, electro-chromism and adsorption of metal ions) (Chen *et al.*, 2016).

In recent years, researchers have started to consider developing materials combining sensing, actuation, computation and communication capabilities. The result of such a high degree of coupling is named *robotic materials*, which have the potential to become the next generation of smart composites (McEvoy and Correll, 2015).

Nanocomposites Enabling Novel Functions

Many actuation, sensing and other functions discussed above are enabled by the incorporated nanoparticles. Functional nano composites are also occasionally referred to as smart composites. For example, synthesized Fe_3O_4 -multiwalled carbon nanotubes are a type of smart composite as they can be used to fabricate intelligent microwave-absorber materials (Lu *et al.*, 2015). Nanocapsules containing functional substances may also be regarded as smart composites when they are applied to the fabrication

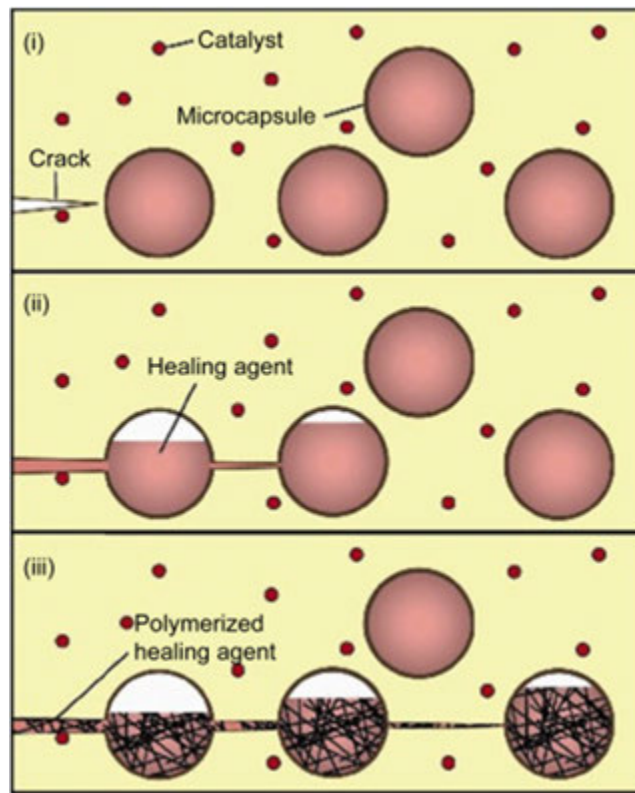


Fig. 5 An example of capsule-based self-healing composites. Reproduced from White, S.R., Sottos, N.R., Geubelle, P.H., *et al.*, 2001. Autonomic healing of polymer composites. *Nature*, 794–797.

of smart coatings for anticorrosion (Wang *et al.*, 2015a) and self-healing (Blaiszik *et al.*, 2008). Carbon fibers can be functionalized with ZnO nanowires so that the synthesized fibers can act not only as a piezoelectric strain sensor, but also as a chemo-resistive gas sensor (Calestani *et al.*, 2017).

The Pillars of Smart Composite Developments

Tposite developments: fundamental physical science and fabrication techniques.

Advances in the Understanding of Fundamental Physical Science

Three major aspects of fundamental physical science contribute to the design of new smart composites: key materials and structures; interfaces between different materials; and composite materials as a system.

Key materials and structures

Understanding key materials and structures usually plays a core role in the development of new functions of smart composites. For example, investigations into graphene and carbon nanotubes have revealed their exceptional physical properties. Such understandings accelerate their adoption in the development of smart composites (e.g., artificial skin (Tao *et al.*, 2017; Tian *et al.*, 2014); self-healing composites (Wang *et al.*, 2016; Liu *et al.*, 2013); materials for de-icing (Zhang *et al.*, 2013; Chu *et al.*, 2014)). A smart honeycomb architecture has a negative Poisson's ratio (Abramovitch *et al.*, 2010). Correct use of this architecture would require an in-depth understanding of its properties and limitations.

Interfaces between different materials

The integration of a number of different materials may require them to bond, which may cause complex interface problems. For example, carbon nanotubes have outstanding thermal properties; adding them to structural composites can help to regulate the thermal behavior of structures (Chu *et al.*, 2014). However, this may also weaken the interlaminar strength of a laminated structure and reduce its mechanical performance (Wang *et al.*, 2016). Taking advantage of the electric alignment behavior of short carbon fibers can produce fiber-reinforced composites that contain aligned short fibers. The strength of this type of material heavily relies

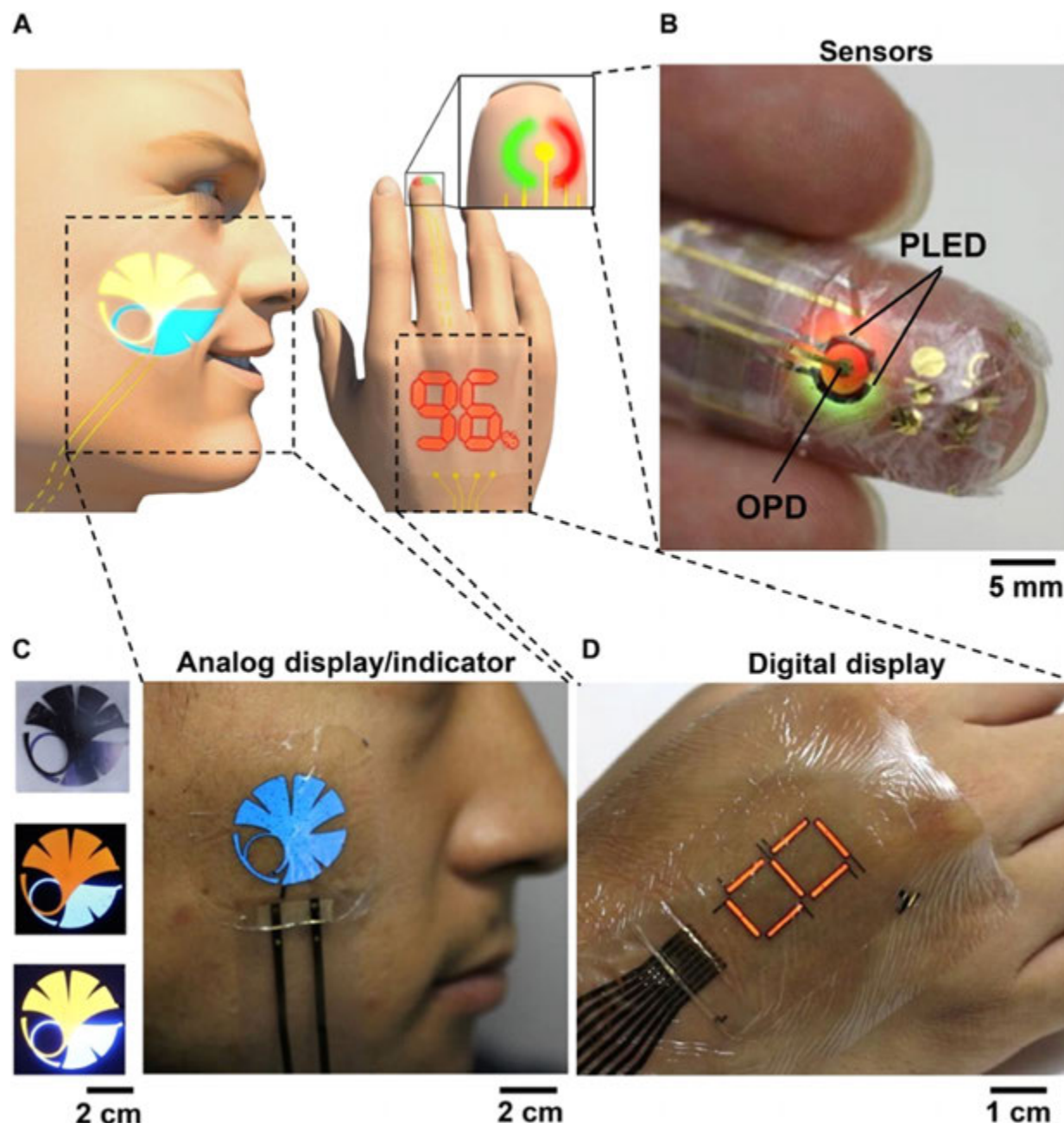


Fig. 6 Smart e-skin system comprising health-monitoring sensors, displays, and ultraflexible PLEDs. (A) Schematic illustration of the optoelectronic skins. (B) Photograph of a finger with an ultraflexible organic optical sensor attached. (C) Photographs of a human face with the blue logo of the University of Tokyo and two-color logos. The brightness can be changed by the operation voltage. (D) Photograph of red seven-segment PLEDs displayed on a hand. Reproduced from Yokota, T., Zalar, P., Kaltenbrunner, M., *et al.*, 2016. Ultraflexible organic photonic skin. *Sci. Adv.* 2 (4), e1501856, with permission.

on the interfacial bonds between the aligned fibers and the matrix (Wang, 2017). The aim of studying interactions between different materials is to maximize the desired performance and minimize negative effects.

Composite materials as a system

In some cases, a smart composite's function has a complex mechanism. For example, the performance of extrinsic self-healing using embedded microstructures is dependent on a number of factors such as temperature, humidity and pressure. Such a high-level complexity cannot be studied using conventional material modeling tools. An alternative is to view composites as systems, and thus tools such as statistical analysis can be employed. There is also an immediate need for computational tools and methods so that the performance of the tools can be maximized.

Advances in Fabrication Techniques

Another pillar of the development of smart composites is their fabrication techniques. Many smart composites have complex structures and patterns. The development of fabrication techniques to produce patterns and alignments in smart composites is considered key to the commercialization of smart composites. For example, optical lenses with tuneable focuses rely on laser manufacturing techniques to create special and accurate patterns (Deng *et al.*, 2015). Building micro hollow structures inside composite materials has benefited from advances in high-precision 3D printing techniques (Bellan *et al.*, 2012).

There have been a number of creative approaches that have been proposed. For example, biomimetic 4D printing has been used to fabricate composite hydrogel architectures that are encoded with controllable functions by the alignment of micro fillers (Sydney Gladman *et al.*, 2016). This technique can be used to fabricate highly stretchable, shape-memory and self-healing elastomers (Kuang *et al.*, 2018). Flexible and conductive sensing components can be produced directly on flexible surfaces by pencil drawings (Liao *et al.*, 2015). With more functions being added to smart composites, demands for accurate, flexible and nano-level manipulation techniques will grow in the foreseeable future (Zhang *et al.*, 2013). Electrostatic discharge was also proposed to fabricate complex networks rapidly. Rapid discharge is similar to lightning, which can create a tree-shape branched network (Huang *et al.*, 2009).

However, the cost of fabrication and the controllability of the fabrication process are critical factors in the development of smart composites. In fact, it has been emphasized in a number of scientific reviews that the speed, cost and reliability of fabrication techniques are the key factors in the application of smart composites (Patrick *et al.*, 2016; Leng *et al.*, 2011; Park *et al.*, 2013).

Major Benefits of Smart Composites

Smart composites have received attention because of their novel functionalities. Existing applications of smart composites suggest that the primary benefits of using smart composites are *their availability, reliability, and capability to extend design freedom*.

Availability

Smartness has never been a more popular word than it is today. Electronic devices such as phones and watches can be smart, and there is a desire for smarter living by improving our homes, buildings, traffic and energy systems. The foundation of smartness in many ways is the availability of information about the operation and condition of a system.

It has been considered acceptable to obtain information through periodic checks and inspections. Today, for those applications requiring continuous operation and monitoring (e.g., wind turbines and power transmission infrastructures), continuous availability of information flow is highly desired. Sensitive structural composites offer an integrated approach allowing direct reading of relevant information (e.g., stress, temperature, humidity).

Artificial skins and wearable textiles give online access to information about body motion and health condition. They may also become the information exchange media to obtain brain information in the future.

Reliability

Novel functions such as self-healing and self-cleaning extend the service life of a structure. An experiment showed that a self-healing capability can stop the incremental deterioration of polymeric materials. In the case of severe fatigue loading, the life of a self-healing polymeric material can be up to 30 times longer than that of a similar but non-self-healing polymer (Jones *et al.*, 2007).

The availability of information improves diagnoses and simplifies maintenance procedures. For example, structural health monitoring techniques based on smart composites are essential for the reliability of military aircraft (Baker *et al.*, 2004).

The mechanisms of functional membrane composites (e.g., separation of different types of liquids) can be more reliable and straightforward than those based on mechanical and cognitive efforts. The adoption of shape-memory composites to deploy space components avoids using mechanical and electrical devices which may be affected by low temperature, vacuum and electromagnetic interferences, and again improves reliability.

Design Freedom

Smart composites possess novel functions because of their useful elements, which offer unlimited flexibility in designing the combination of these functions. For example, the self-healing elements of an extrinsic self-healing composite are the embedded microstructures (e.g., capsules and vessels); the elements of a sensing composite are the electronic and conductive components. Using both functional components in a composite allows it to heal and sense (Swait *et al.*, 2012). In the case of a crack, the composite may recover not only its mechanical strength but also the connectivity of its sensing components (Wang, 2017).

However, it is worth noting that mixing functionalities may cause undesired effects. For example, novel composites incorporating self-heating components can de-ice automatically (Chu *et al.*, 2014). However, using such a design could weaken the interlaminar strength of materials in the context of fiber-reinforced composites (Wang *et al.*, 2016).

Developments in Smart Composites

Developments in the field of smart composites can be explained using the Patterns or Trends of Technological Evolution discovered by Altshuller, the founder of the Theory of Inventive Problem Solving (TRIZ). Altshuller suggested that technological systems evolved not randomly but rather followed a number of predictable trends (Zlotin, 2013):

- (1) Stages of evolution (infancy, growth, maturity, and decline). This pattern explains the two key stages of technological development.
- (2) Evolution towards increased ideality. The definition of ideality is given in Zlotin (2013): ‘...Ideality for a given system can be defined as the ratio of the sum of its useful features (benefits) to the sum of harmful (or undesired) factors. Therefore, a system’s ideality can be increased by increasing its useful features, reducing the harmful ones, or both.’
- (3) Non-uniform development of system elements. Different components of a technological system develop at different paces. A component on a slow-pace development trajectory can be the bottleneck in the progress of an entire technological system.
- (4) Evolution towards increased dynamism and controllability. Technological systems become more dynamic in their evolution, and allow better controllability.
- (5) Evolution towards increased complexity followed by simplification. A technological system increases its complexity by incorporating more functions and applications, and the complexity reduces as the integration is optimized.
- (6) Evolution with matching and mismatching elements. An evolving system’s elements and components are matched or mismatched to improve performance or mitigate undesired effects.
- (7) Evolution towards micro/multi-levels and the increased use of fields. Systems evolve towards the micro-cosmic level by taking advantage of more sources of energy (e.g., mechanical, thermal, electrical, magnetic, molecular and chemical).
- (8) Evolution towards decreased human involvement. Systems become more autonomous and intelligent.

The development of smart composites reflects most of the above trends. For example, shape-memory composites have increased in dynamism and controllability (i.e., controllable shape-changing dynamics, trend 4), used multiple energy sources (e.g., thermal, optical, electrical, trend 7), and become able to change shape autonomously (Trend 8). The development of shape-memory composites can also represent trend 5, as a shape-memory actuator is simpler than a conventional mechanical actuator. Similar trends can also be seen in other types of smart composites.

Smart composites are also the enabler of many technological evolutions on the application level. For example, the trend in aircraft development is increased dynamism and controllability (trend 4). The ability to morph, i.e., transform shapes or structures, can allow an aircraft to operate in a wide range of conditions and environments (Barbarino *et al.*, 2011). This capability relies on the active shape changing of smart composites.

These trends also suggest possible future directions in the development of smart composites. Trend 2, evolution towards increased ideality, indicates that creating useful functions should outweigh the undesired effects that come along (e.g., high cost, reduced reliability and weakened strength). Trend 3 indicates that the development of smart composites should focus on key problems in the machine or system of which they form a part.

Summary

Smart composites are a group of composite materials that can react to external stimuli in controllable ways. This research field has undergone rapid growth in the past three decades. Typical smart composites include sensitive structural composites, composites for actuation, composites with novel functions, and nanocomposites enabling novel functions. Smart composites have the potential to improve the availability of data and information, enhance the reliability of a material system and deliver multifunctional applications. Advances in smart composites rely on investigation into fundamental physical science and better fabrication techniques.

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Composite Metamaterials: Types and Synthesis

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Nomenclature

ALD Atomic layer deposition
CMM Composite Metamaterial
CVD Chemical vapor deposition
DEW Direct electrochemical writing
ELD Electroless deposition
FIB Focused ion beam
IP Inkjet printing
MLD Molecular layer deposition
MM Metamaterial

PMMA Polymethylmethacrylate
PS Polystyrene
PVD Physical vapor deposition
SL Stereolithography
SLM Selective laser melting
SLS Selective laser sintering
SRR Split-ring resonator
TAE Template-assisted electrodeposition
TPL Two-photon lithography
μSL Microstereolithography

Glossary

Auxetic materials Materials with a negative Poisson ratio, therefore contracting upon compression.

Composite Metamaterials Materials featuring a microstructure or architecture to create exotic properties.

Photonic crystal Structures featuring a repetitive feature with the periodicity in the range of visible light, creating a bandgap in this periodicity.

Split-ring resonator Metallic rings featuring a gap in each ring, creating a low resonance structure.

Two-photon lithography Lithography technique using a laser at twice the wavelength of the absorption band of the photoresist, localizing the chemical reaction to the focal point. This allows for 3D micro-printing.

Introduction

Metamaterials

Metamaterials (MM), artificial composite structures with exotic material properties, have emerged as a new frontier of science involving physics, material science, engineering, and chemistry. Recently, MMs have been described in a more broad term as structures with an imposed geometry to fit an intended use.

MMs have emerged as a new promising class of architected materials with advanced multi-functional properties. The properties of such 3D architected structures are a combination of the architecture, the size of features within the architecture, the microstructure and the inherent properties of the material, as can be seen in [Fig. 1](#). Introducing architecture can significantly alter some material properties and can even introduce the aforementioned exotic properties, such as negative refractive indices, negative thermal expansion, negative Poisson ratio and photonic bandgaps amongst other properties.

Composite materials can be defined as materials that consist of two or more chemically and physically different phases separated by a distinct interface. The creation of composite metamaterials (CMM) allows, on one hand, to influence the microstructure level and the introduction of an imposed geometry can introduce new or optimized material properties not achievable with bulk material. Overall, CMMs significantly enlarge the design space of MM.

Nowadays architected structures, MMs and CMMs are already incorporated, or on the verge of incorporation for industrial applications in photovoltaics, microelectromechanical systems, lightweight materials, mechanics, energy storage and sensing devices. Additionally, the scientific community has started to use complex microscale architectures as experimental setups in microfluidics and biology.

MM Applications

CMMs are extremely promising candidates for applications in various fields from photonics, acoustics, mechanics, electromagnetics, and sensing which all make CMM extremely interesting for MEMS applications and micro-robotics.

The new era of CMMs lays within the microscale, as the application of such materials in MEMS devices and micro-robotics is spatially constrained. Furthermore, substantial amounts of non-mechanical MM applications reported in the literature are based on architected microstructures. Therefore, the metamaterial research is highly interdisciplinary ranging from mechanics, photonics, and acoustics to sophisticated micro- and nanofabrication.

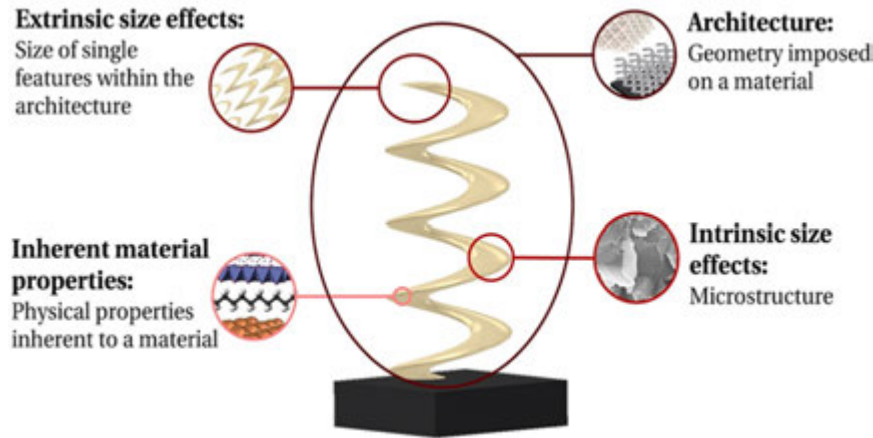


Fig. 1 Influences on the material properties of a metamaterial.

Text Body

Mechanical metamaterials

In mechanics, MMs have drawn attention due to their highly exciting and tunable properties. Negative and near-zero Poisson ratio materials are known as auxetic and anepirretic materials respectively. These metamaterials exhibit compression upon loading (Lakes, 1993; Buckmann *et al.*, 2012; Yuan *et al.*, 2019), a highly interesting phenomenon leading to increased shock absorbance, indentation resistance, and shear resistance. Due to these properties, these materials are often used in protective gear, but also proposed for medical devices such as stents, or other applications such as gaskets and air filters. While α -cristobalite Si is a natural occurring auxetic material (Alderson and Evans, 2002), most other reported auxetic materials get the auxetic property from the geometrical design (Stavric and Wiltse, 2019; Hengsbach and Lantada, 2014). In the case of composites, the composition and distribution of the different phases (Alderson *et al.*, 2005) can be arranged to yield auxetic material. The design of auxetic composite materials has been well studied. In general, auxetic composites can be produced by using auxetic components such as auxetic host material or auxetic fiber reinforcement of a host material (Alderson *et al.*, 2005).

Another focus of mechanical MM is the possibility of high strength/lightweight materials. Taking a look at the Ashby plot comparing strength versus density, see Fig. 2(a), most materials follow the trend of strength through additional weight. Materials with high strength but lightweight aim to fill the voids in the diagram by maintaining the strength of the bulk materials and reducing the density significantly. Ashby introduced a set of rules on the deformation depending on the architecture. He determined which architecture would be ideally suited to carry a large load, depending on Maxwell's stability criterion (Ashby, 1983, 2013; Deshpande *et al.*, 2001a,b). In general, in an open-cell foam structure, the compressive modulus scales with the density of the structure to the power of 3, due to the inefficiency of the system. In more aptly designed structures, see Fig. 2(b) and (c), the compressive modulus scales to the relative density squared. These materials are of special interest for high strength/low weight applications (Deshpande *et al.*, 2001a). In well-designed structures with more conjoined struts, the compressive modulus scales linear to density. Composite materials, such as nanoparticle or fiber-reinforced composites offer a high bulk strength. These composites are prime candidates for high strength/lightweight materials, as the strength can be retained while the weight can be reduced through 3D structuring.

While both, auxetic and high strength/lightweight phenomenon can be observed at the macroscale, microscale mechanical MMs have drawn significant interest as well. In the microscale, the mechanical properties of structures start to change. So-called intrinsic and extrinsic size effects, which are especially pronounced in metallic materials, have been shown in lattice structures for polymer-based CMM micro-lattices (Bauer *et al.*, 2014; Mieszala *et al.*, 2017).

Other less mentioned mechanical MMs are nonlinear materials with have mechanical anisotropy (Florijn *et al.*, 2014; Huber, 2016; Coulais *et al.*, 2016; Coulais *et al.*, 2017), programmable materials (Florijn *et al.*, 2014; Silverberg *et al.*, 2014), and zero thermal expansion composites (Qu *et al.*, 2017).

Photonic metamaterials

In photonics, MMs are being created to control the path of light. Photonic bandgaps (Teyssier *et al.*, 2015), negative refractive indices (Soukoulis *et al.*, 2007; Rill *et al.*, 2008) and polarization filtering (Gansel *et al.*, 2012; Kaschke *et al.*, 2012, 2014; Kaschke and Wegener, 2015) are amongst the properties that can be induced by imposing a certain geometry.

Negative refractive index materials and so-called left-handed media materials (Veselago and Narimanov, 2006) have drawn a lot of attention since the concept was developed by Veselago (1968) – A possible material was theorized by Pendry *et al.* (1999) and first proven experimentally by Smith *et al.* (2000). This MM property opens up the possibility of creating materials with reversed Doppler effect, electromagnetic camouflage, superlenses (Enoch *et al.*, 2002) and optical tunneling (Edwards *et al.*, 2008). The most used structures to create these effects, also the once above mentioned theorized and proven, are split-ring resonators (SRR), see Fig. 3(a). SRRs usually consist of non-magnetic, interleaved metal rings on a non-metallic substrate. They are therefore

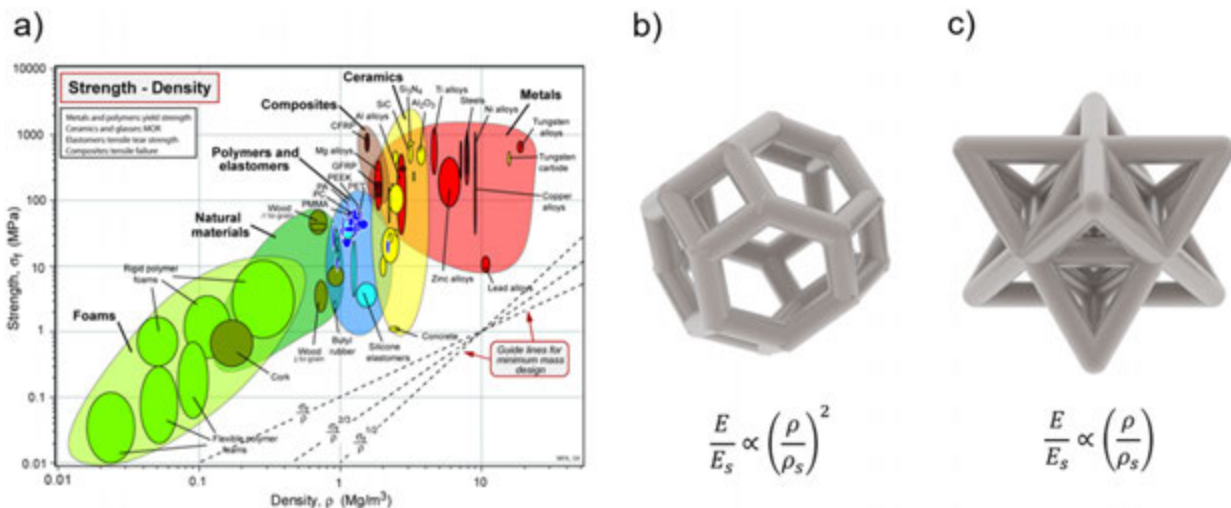


Fig. 2 (a) Ashby plot strength vs density. (b) bending-dominated kelvin foam. (c) a stretching dominated octet structure. E is the youngs modulus of the structure and E_s the youngs modulus of the bulk material the structure is made of. ρ is the density of the structure and ρ_s the density of the bulk material the structure is made of.

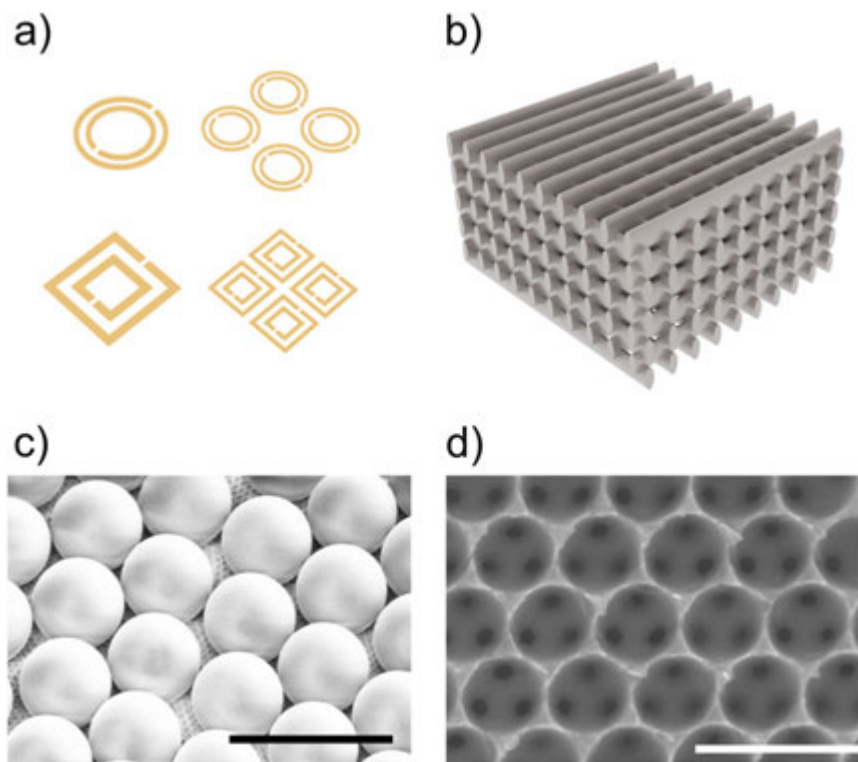


Fig. 3 The most common designs for photonic MMs: (a) SRRs, (b) woodpile structures, (c) colloidal crystals, and (d) inverse opals. Size indicator 10 μm in (c) and 1 μm in (d).

composites by definition (Smith *et al.*, 2000). If exposed to an outside magnetic field, the introduced current in the rings creates an electromagnetic field. The gap, or gaps depending on the design, has a large capacitance, which influences the resonance frequency. The configuration results in structures with a very high quality factor. Cloaking applications are often mentioned for the SRRs, due to the creation of an opposing flux to the incident one.

The introduction of a repetitively layered structure in a 3D material can create a photonic bandgap (Purcell, 1946; Yablonovitch, 1987). Light with a wavelength matching the distance between the layers cannot pass through the structure and is reflected. These so-called band-stops attracted large scientific interest to create optical networks akin to electrical networks in semiconductors. The most prominent

designs are so-called woodpile structures (LaFratta *et al.*, 2007; Mizeikis *et al.*, 2007; Nagpal *et al.*, 2008; Walsh *et al.*, 2009; von Freymann *et al.*, 2010), due to relatively simple design, see Fig. 3(b). Colloidal crystals have drawn attention due to the relatively simple fabrication methods by self-assembly, see Fig. 3(c). These self-assembled structures can be used as templates, the voids can be filled and inverse opals can be created, as can be seen in Fig. 3(d).

Chiral structures used to control the polarization of light have attracted much attention as well. Optically active materials, such as gold and silver were used in multiple studies to create such polarizers. Gansel fabricated such polarizer with template-assisted electrodeposition (TAE) from pure electrodeposited gold (Gansel *et al.*, 2012, 2009) while others covered the two-photon lithography (TPL) prints with silver by electroless deposition (ELD) (Yan *et al.*, 2011).

All of these previously mentioned MMs have been well-studied and are moving towards applications. More recently, optical switching CMMs have been developed. For example, thermoresponsive nanoplasmonic switches made from organic surface-modified gold nanoparticles on metallic substrates (Ma *et al.*, 2019).

Acoustic metamaterials

Acoustic MMs, usually rely on a geometrical design to control sound wave propagation. The same ideas as for photonic MMs can often be applied, because of the similar behavior of the electromagnetic and acoustic waves.

Phononic crystals, which are conceptually similar to photonic crystals, are one kind of acoustic MMs. A multitude of 2D phononic crystals were reported, able to filter phonons of a certain wavelength due to the induced bandgap. Most phononic crystals are made from silicon with a well-designed array of holes (Sledzinska *et al.*, 2016; Wu *et al.*, 2005). Phononic crystal composites can also be fabricated, for instance, al-pillar arrays on silicon (Sledzinska *et al.*, 2016). More intricate designs, such as piezoelectric composite material/kapton stacks have also been reported. The piezoelectric response allows changing the phononic bandgap (Croenne *et al.*, 2016). 3D phononic crystals have been produced as well, with stereolithography designs made out of acrylic polymer. Composites were created from 3D printed polymer and metallic components, which offer a more elaborate design space for broadband vibration propagation.

Silencers or cloaking MMs have been proposed based on other designs than SRRs or phononic crystals. Fano-like dampening was used to create a silencer from polymer (Ghaffarivardavagh *et al.*, 2019). Others have produced silencers with inertial local resonant structures for acoustic lensing (Bigoni *et al.*, 2013).

Metamaterials for sensing technology

A large field of active MEMS-device research focuses on developing new, reliable, and highly reactive sensors. In particular, SRRs, due to their high quality factor, have enormous potential in sensing applications and are currently the most investigated. Since their introduction in 1999 (Veselago and Narimanov, 2006; Veselago, 1968), SRR arrays have been proposed as sensors for various applications due to their negative permeability and permittivity. Arrays of SRRs have been used as sensors for mechanical strain, temperature, deposit thickness, gas detection and concentration sensing, microwave, and molecule detection (Chen *et al.*, 2012). The detection works by sensing a change in resonance frequency. The SRR can be considered as LC-oscillator. The resonance frequency, f , can be calculated as:

$$f = \frac{1}{2\pi\sqrt{LC}}$$

where L is inductance, and C is the capacitance, which is mainly given by the narrow gap sections.

The SRR resonance frequency can be altered by changing the capacitance or inductance of the resonator. For instance, temperature changes influence the dielectric constant of the substrate material and therefore the resonance frequency (Vena *et al.*, 2015). Mechanical deformation causes the capacitance to change due to the geometrical change in the narrow gap region. Microfluidic molecule sensing was done by introducing a microfluidic channel on top of an SRR to induce a resonance frequency change upon molecular adsorption (Salim and Lim, 2016). Gas sensors were built by introducing a conductive polymer within the SRR to change the dielectric constant on the adsorption of the gas in the polymer (Vena *et al.*, 2015). For bio-sensing, the SRRs can be coated with a biochemical receptor which allows the sensing of the acceptor (Lee *et al.*, 2008; Jaruwongrungrueng *et al.*, 2015). The resonance frequency change could eventually even be enhanced by 3D structuring of the SRR in the sensors (Decker *et al.*, 2010). The number of scientific publications about SRR sensing applications indicates that the technology is ready to be taken from MMs to meta-devices.

The previously mentioned colloids and inverse opal structures have also shown promising results as gas sensors due to high surface area and tunable conductance based on gas adsorption (Cantalini *et al.*, 2005).

Metamaterials in micro-robotics

Most published micro-robots fulfill partially or fully the conditions to be called CMMs. Movement in these micro-robots is achieved through the presence of anisotropy in the design, which can be introduced through the shape but also through a change in material, which makes CMMs prime candidates for micro-robotics applications. A multitude of studies were pursued on magnetic micro-robots (Serra *et al.*, 2015; Garcia-Torres *et al.*, 2017) but also chemical propulsion has been studied (Paxton *et al.*, 2006).

For magnetic propulsion, a common approach is to study polymeric 3D structures that are covered with a magnetic material. For instance, TPL spirals were covered with e-beam evaporation of nickel and titanium, and nickel sputtering (Barbot *et al.*, 2016).

and subsequently moved through magnetic field manipulation. For catalytic propulsion, nanorods and cones have mainly been used. The nanorods are usually segmented, for instance with a gold and platinum segment as done by Paxton *et al.* (2006). The segmentation creates different domains on which, in the host medium, different reactions take place, propelling the rod onwards. These kinds of micro-robots have various applications such as environmental cleaning devices (Serra *et al.*, 2015; Garcia-Torres *et al.*, 2017) or cargo transport as possible drug delivery systems (Nelson *et al.*, 2010; Barbot *et al.*, 2016).

Synthesis of CMMs

Additive Manufacturing

Additive manufacturing offers multiple benefits to create CMM: improved sustainability by lowering the resource effort, increased design freedom, manufacturing to demand and a resolution window from the macroscale into the nanometer scale. As already mentioned, a multitude of MM applications require microscale structures and are therefore difficult to produce with subtractive methods. Additive manufacturing methods are already implemented in the automotive, machining, aerospace, electronics and medical products, which are also the industries with possible applications of CMMs (Ford and Despeisse, 2016). Additive manufacturing is the most suitable path, considering small batch manufacture, prototyping, research and development of CMMs (Thomas, 2016).

Methods and Size

In the macroscale, additive and subtractive methods are used to produce MMs and CMMs. From micromachining to established mesoscale additive manufacturing like selective laser melting (SLM) and sintering (SLS) are used to create CMM. In the microscale, subtractive methods with the necessary resolution become rare and the available methods such as focused ion beam (FIB) milling are directional with a limited degree of geometrical freedom.

However, the resolution of the chosen additive manufacturing method is crucial to create a metamaterial with the desired properties. While negative Poisson ratio, zero thermal expansion, mechanical nonlinearity, and programmable mechanical MMs are size-independent, other metamaterial applications are size-dependent. Applications, depending on effects such as artificial bandgap in optics and acoustics, the resonance frequency of SRRs require manufacturing in the appropriate size range. Furthermore, uses in MEMS-devices and micro-robotics also require microscale manufacturing.

The resolution of additive manufacturing methods are compared in Fig. 4. While all of the listed manufacturing methods can be used to CMMs, each has a specific resolution and, therefore, a specific size range in which the structures can be produced. In 3D printing, the resolution is usually described as voxel size. The voxel is the size of an addressable volume, analogous to the pixel in 2D. The voxel size is crucial in which size scale the method is applicable. A small voxel allows for the creation of smaller, more intricate structures whereas a larger voxel enables the creation of macroscale structures in reasonable time scales.

Material dependent aspects of the process must be taken into account as well. While all the techniques listed in Fig. 4 can be used to produce a multitude of polymers, metal, alloys, and semiconductors depending on the metal itself, certain material limitations can occur.

It is therefore important to choose a manufacturing method able to produce the materials of choice in the desired size scale with the desired geometry.

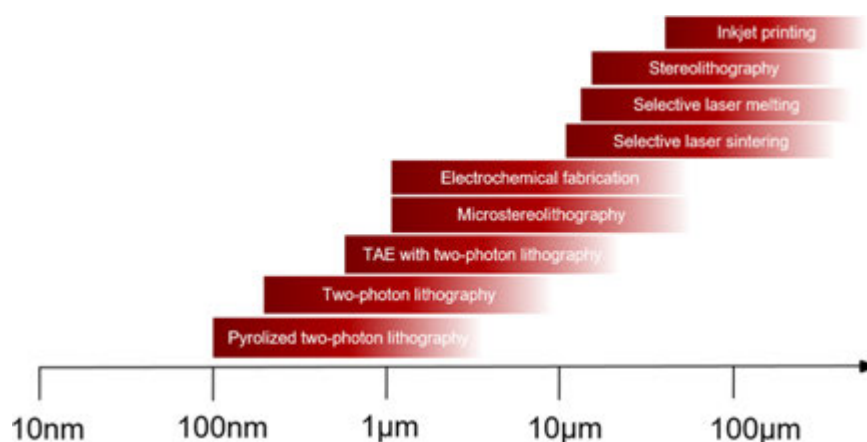


Fig. 4 Lowest averaged resolution (voxel or pixel dimensions) of different additive manufacturing techniques. A table of the publications used to create this figure can be found in the supporting information, see Supporting Information Table 1.

A list of selected CMMs, their applications, the materials, and the used manufacturing techniques can be found in the supporting information, see Supporting Information Table 2.

Selective Laser Melting (SLM) and Sintering (SLS)

Macroscopically, selective laser melting (SLM) and sintering (SLS) of metal or alloy powder have been well established. The microscale versions of the processes have gained attention because by reducing the laser spot size and powder diameter it has been possible to venture further into the microscale. Due to the larger voxel size, mechanical and acoustic metamaterials are the most prevalent ones among the MMs produced with this method. Selective laser melting has been used in multiple studies to create micro-lattices from stainless steel 316 (Bonatti and Mohr, 2019; Tancogne-Dejean and Mohr, 2018), high strength steel 4130 (Li *et al.*, 2019), and titanium (Wei *et al.*, 2018). A multitude of particle reinforced SLM composites has been investigated on non-metamaterials, mainly for strengthening the structures through inclusions of the nanoparticles, showing that the method is suitable to create CMMs. Selective laser sintering for MMs is mainly used to create mesoscale polymeric structures from polyurethane and nylon (Yuan *et al.*, 2019; Shen *et al.*, 2016; Yuan *et al.*, 2017). However, also sintered composites have been reported (Yuan *et al.*, 2019).

Inkjet Printing (IP)

IP is a cheap and reliable method for creating macroscale to mesoscale 2D CMMs. IP has been used frequently to create SRRs on flexible substrates, where a suspension of nonmagnetic nanoparticles is being placed on a substrate and afterward sintered into a conductive metal. Therefore, most printed materials should be sintered at low-temperature while the mostly flexible polymer substrates must withstand the sintering temperature. The creation of the ink must be attuned to the resolution that is aimed for, as each droplet must contain the binder, adhesion promoters and sufficient amount of suspended nanoparticles. The suspension stability can be improved by adding dispersants. Most inkjet printed SRR are single ring SRRs with a diameter of over 100 μm . As SRRs are the most common CMMs, this technique has been employed frequently (Vena *et al.*, 2015; Walther *et al.*, 2009; Kashiwagi *et al.*, 2018).

Direct Electrochemical Writing (DEW)

Electrochemical additive manufacture methods are an interesting alternative to other techniques as they allow to reach the microscale in a relatively cheap manner as most of these processes are operated at ambient or slightly elevated temperature and ambient pressure. A counter electrode and a working electrode are immersed in an electrolyte containing ions of the elements that are to be deposited. The electrodeposition takes place as a current is applied or a potential is applied between the electrodes. The main deposition parameters are the applied current and potential and the electrolyte composition as well as temperature and convection.

DEW uses a needle as an anode to induce deposition locally on a working electrode substrate. The electrodes can be immersed in an electrochemical bath and the electrodeposition area is given by the current distribution and electrolyte concentration (Seol *et al.*, 2005; El-Giar *et al.*, 2000). A more localized version of 3D electrochemical writing was used by Hirt *et al.* (2016). The electrolyte is pumped through the anode needle into a supporting electrolyte media shortly before the pulse is applied. Micro-lattices and helices, see Fig. 5(a), have been produced.

Otherwise, a droplet of electrolyte can be placed between the working and counter electrode to have the meniscus confining the electrodeposition (Daryadel *et al.*, 2018; Yi *et al.*, 2017). This technique has so far been used to create simple 3D acoustic structures like antennas (Daryadel *et al.*, 2018; Yi *et al.*, 2017).

Stereolithography (SL) and Two-Photon Lithography (TPL)

Stereolithography (SL) and Microstereolithography (P μ SL) are techniques where a light source at a wavelength of 395 nm is focused into a photoresist to induce a chemical reaction in the photoresist to crosslink or decompose parts of the photoresist molecules. There is a multitude of SL systems, which use a layer-by-layer based approach to cure a part made from photoresist. SL resolution is frequently reported to achieve to layer heights of 25 μm or bigger, P μ SL can reach resolutions of 1.3 μm and a layer size of 300 nm (Zheng *et al.*, 2012). SL is therefore mainly used to create mechanical MMs (Tumbleston *et al.*, 2015), while P μ SL can reach dimensions used in other MM applications.

The TPL technique is an advanced type of SL and is built upon the two-photon absorption effect, first described by Nobel prize Laureate Maria Goppert-Mayer (Goppert-Mayer, 2009). The absorber molecule absorbs at a higher energy than the laser, so the chemical reaction is initiated only in the focal spot, where the possibility of multi-photon absorption is given. During two-photon absorption, a molecule simultaneously absorbs two photons that induce an electronic transition from a ground state to an excited state inaccessible by single-photon absorption. The two-photon absorption triggers the local chemical reaction in the photoresist. Moving the laser at will through the photoresist allows for freeform 3D shaping. The two-photon absorption retains the reaction

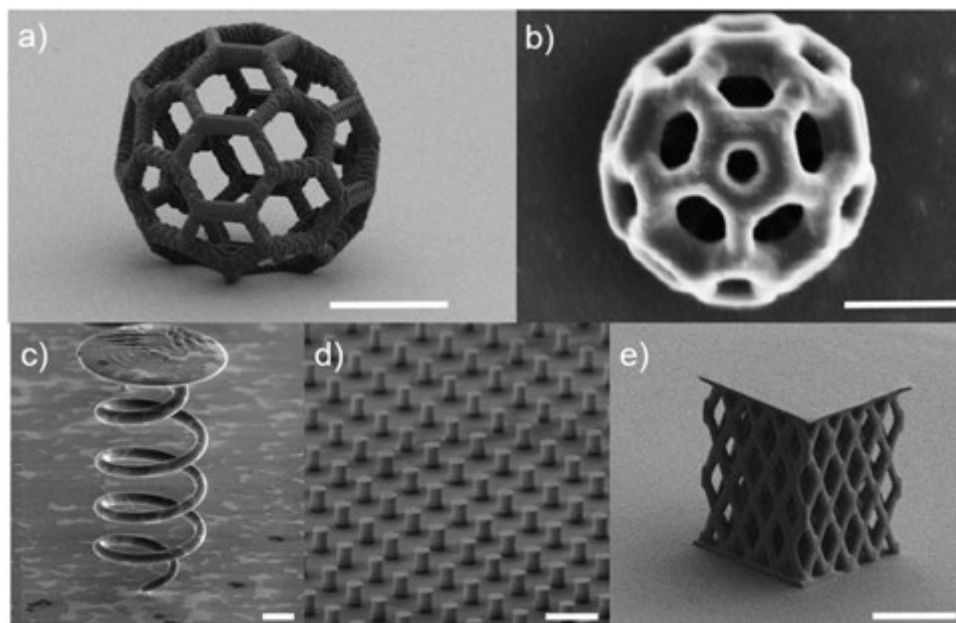


Fig. 5 (a) IP-Dip photoresist buckyball printed on ITO, (b) Pyrolyzed IP-Dip photoresist buckyball (Courtesy of Petai Pip), (c) Copper spiral DEW (Courtesy of Dr. Ramachandramoorthy and Exaddon GmbH), (d) and (e) nanocrystalline nickel structures produced by TAE. Size scale indicators 20 μm for (a), (c), (d), (e) and 1 μm for (b).

localized to the focal point, increasing the resolution and allowing for true 3D printing, while there is still the possibility to write with a layer-by-layer approach.

Two main categories of photoresist can be used. Negative-tone photoresists, such as SU-8, IP-Photoresists (Nanoscribe GMBH), ORMOCORP and positive-tone photoresists such as the AZ XT series (Hoechst chemicals). In the negative photoresist, the laser crosslinks the monomer in the resist, subsequent developing is used to remove the non-reacted photoresist. In positive-tone photoresists, the illumination decomposes a photoactive compound and the subsequent development can dissolve the photoresist where it was illuminated.

Other non-commercial photoresist has been reported. An interesting approach is to directly add metal-organic compounds into the resist, which agglomerate and create a metal/carbon framework after pyrolysis, as a way to directly write a composite CMM (Vyatskikh *et al.*, 2018). Ceramics precursor can be used as well that turns into the ceramic after pyrolysis, which has been reported to have a resolution down to sub-100 nm features (Gailevicius *et al.*, 2019).

Multiple different ways can be used to produce CMMs from stereo- and multi-photon lithography, as can be seen in Fig. 6. The printed structure made out of photoresist can be functionalized with electroless deposition (ELD), atomic layer deposition (ALD), chemical vapor deposition (CVD) or physical vapor deposition (PVD). These are in itself already composites containing the photoresist structure and the coating. However, the coating in itself can already be produced as a composite as well. Afterward, the polymeric backbone can be removed by pyrolysis, leaving a 3D architected hollow CMM. To create non-polymeric, non-hollow MMs, one of the most feasible processes is TAE. A template is written in photoresist on a conductive substrate and, subsequently, filled with an electrodeposited material. After the template removal, a dense metallic or composite architecture is left, which then, in turn, could be further functionalized.

Electroless deposition (ELD)

ELD is a convenient method to coat the surface of 3D micro-printed surfaces in a conformal way (Sudagar *et al.*, 2013). Samples are surface-treated with oxygen plasma and subsequently coated in a catalyst. Afterward, they are immersed in an electrolyte containing the ions that are to be deposited. The catalyst together with a reduction agent provides the electrons necessary to reduce the cations present in the solution, creating a conformal plating (Brenner and Riddell, 1946). The thickness of the metallic layer can be controlled by adjusting the time the sample is exposed to the electrolyte and the amount of catalyst, reducing agent and cations. In literature, ELD is frequently used to create composites (Sudagar *et al.*, 2013) with hard particles such as SiC (Hicks and Dresselhaus, 1993), diamond (Reddy *et al.*, 2000) or others to create hard coatings. Solid lubricants such as PFTE (Balaraju *et al.*, 2003; Huang *et al.*, 2003) have also been introduced into the coatings while others have incorporated various intermetallic, oxide or other particles. The method has been used successfully to coat 3D structures created with TPL in various studies. Especially for optical application, ELD on TPL structures has been used in multiple studies on helices and woodpile structures (von Freymann *et al.*, 2010). Optically active materials such as silver (Yamamoto *et al.*, 2008; Kenanakis *et al.*, 2015) and copper (Tal *et al.*, 2007) have been used. ELD coated micro-lattices with nickel/boron were used to reinforce the lattices (Mieszala *et al.*, 2017).

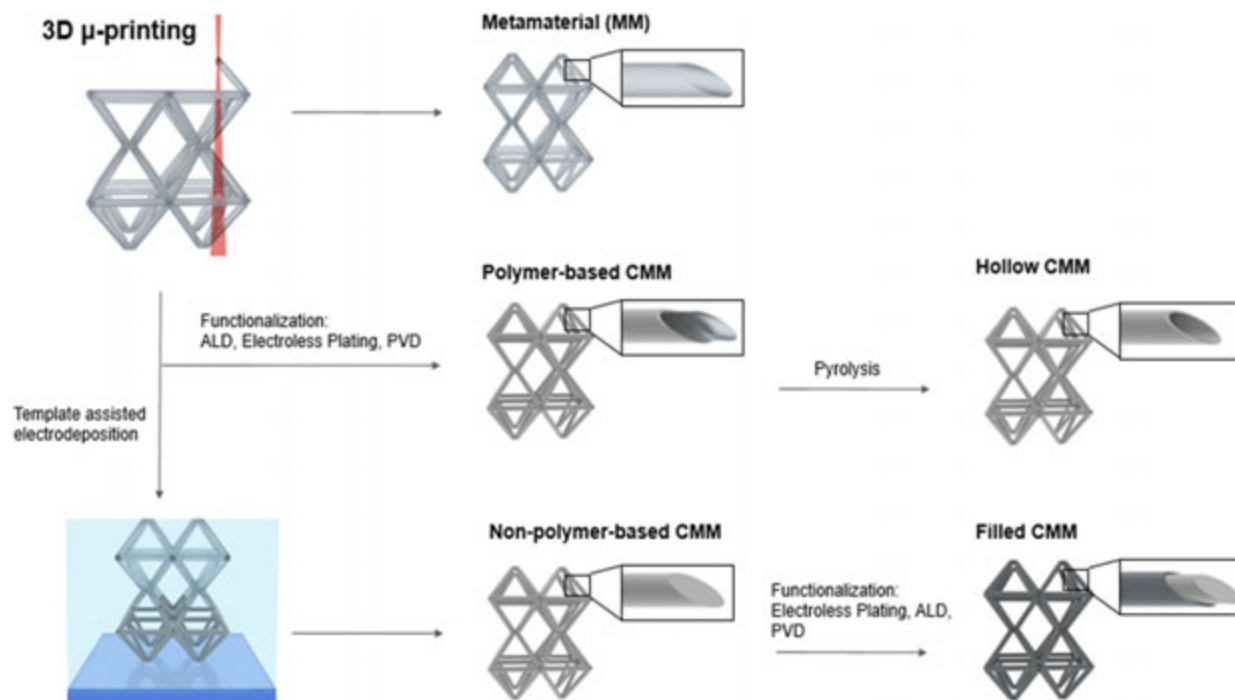


Fig. 6 Pathways to different CMM-types by stereo- and multi-photon lithography.

Atomic layer deposition (ALD)

ALD is a well-established process (Suntola and Antson, 1977; Suntola and Hyvarinen, 1985; Suntola, 1992; George, 2010) to form conformal coatings on complex structures. A layer of gaseous precursor molecule coating the 3D structure is flushed over the sample forming a monolayer of precursor compound on the active sites of the substrate. After a purge, a second precursor is flushed into the chamber, removing the ligands from the first precursor monolayer and adding a layer of active sites for the next cycle. Subsequently, the first precursor is flushed into the chamber to start the cycle again. With this process, monolayer after monolayer can be deposited to create a conformal coating. Different precursors can be used to create multilayered composite coatings.

ALD can create metals and oxides, TiO_2 (Haukka *et al.*, 1993) and Al_2O_3 (Fan *et al.*, 1991) are amongst the most prevalent in literature. Molecular layer deposition (MLD), can also be used for organic surface modification (George *et al.*, 2009). ALD was used in different studies to coat and functionalize 3D micro-printed structures (Bauer *et al.*, 2014). Especially for photonic MM, TiO_2 has been used as a coating to adjust the photonic bandgap of structures (Graunard *et al.*, 2006). Iridium ALD was also reported on tungsten woodpile structures (Walsh *et al.*, 2009).

Chemical vapor deposition (CVD) and physical vapor deposition (PVD)

CVD can be used to cover the 3D micro-printed material and has been used to cover even intricate 3D designs. The deposited metals are introduced as a part of a precursor molecule which during the reaction in the chamber deposits as solid material. From a large range of materials that can be deposited, silver is the most commonly used. Silver was used to cover 3D structures to tune the artificial bandgap (Rill *et al.*, 2008; Nagpal *et al.*, 2008). Due to the nature of CVD, coverage depends on the gas flow through the 3D structure and the reaction rate, which can be hindered through the architecture. This can significantly increase the difficulty to control the homogeneity of the coatings accurately (Nagpal *et al.*, 2008).

PVD is a widely used process to deposit films from a target onto a substrate in a vacuum chamber. With a large number of materials to deposit from metals, oxides, semiconductors, the process is interesting due to the possibility of creating multilayer composites as well as nanoparticle/matrix composites. However, the deposition method is directional from the target to the substrate and therefore shadowing effects from the 3D micro-printed structures occur. Due to this reason, the method is not ideal for coating complex structures. It is suitable, however, for less complex structures and for applications where there is no need for a very homogenous coating. Microlattices covered with CrMnFeCoNi high entropy alloy were produced successfully (Surjadi *et al.*, 2018).

Pyrolysis and oxygen plasma etching

Pyrolysis is used to shrink the printed photoresist by carbonizing the structures. The process involves multiple steps of heating up to 600–1200°C. The structures are reported to shrink to 20% of the initial size, therefore opening new possibilities for the size of micro-printed structures (Bauer *et al.*, 2016). Recently, photoresist containing metal-organic precursor produced metal/carbon

structures with 73% atomic percent metallic nickel content which exhibited metallic mechanical properties (Vyatskikh *et al.*, 2018). The printed structures for pyrolysis need to be placed on a base of photoresist as well, for the substrate of the structure shrinks simultaneously with the initial design.

The structures printed with two-photon lithography can also be etched by reactive oxygen plasma (Gross and Bertoldi, 2019). Compared to the pyrolysis, the overall size of the structure remains roughly the same while reducing the diameter of struts, connections, and filaments in the 3D design.

Template-assisted electrodeposition (TAE)

TAE is based on electrodeposition, where a conductive substrate is used as a working electrode in an electrochemical cell containing an electrolyte and a counter electrode. When a current is passed through the cell, or a potential applied, between the electrodes, ions from the electrolyte are deposited. Template assisted electrodeposition forces the electrodeposition from the conductive substrate through a predefined cavity in a nonconductive coating. Therefore, the benefits of electrodeposition can be used to create a freestanding 3D metallic or oxide structure after the photoresist is removed. Technical challenges arise from the multistep production method and electrodeposition challenges depending on the geometry and its influence on the electrodeposition.

The process has been used to create copper quasi single-crystalline micro-lattices (Gu and Greer, 2015), nickel mesoscale lattices, mechanical test specimen (Schurch *et al.*, 2018), gold helices (Gansel *et al.*, 2012; Kaschke *et al.*, 2012; Gansel *et al.*, 2009) and inverse opals (Wang and Wang, 2008) for photonics. Electrodeposition of composites, such as nanoparticle (Hou and Chen, 2011), nanofiber (Wan *et al.*, 2000) or carbon nanotube (Carpenter *et al.*, 2011) incorporation in a metallic matrix has long been introduced for thin films, it has yet to be used to create CMM.

Lithography

Electrodeposition can be used to fill templates from nanometer to millimeter scale. The choice of the lithography method is key to achieve the desired structure in the appropriate size scale, as the lithography method is the main influence on the resolution of the method. Historically, E-Beam, X-ray, and UV-lithography are the most frequently employed techniques (Becker *et al.*, 1982; Mata *et al.*, 2006; Kupka *et al.*, 2000). These lithography techniques can create 2D and 2D multilayer templates. Other, often used, templates are ion-track etched membranes (Frantz *et al.*, 2012) and anodized alumina pores (Sander *et al.*, 2003). These pores are used to create nanowires or nanowire arrays and offer pore size as small as 10 nm (Martin-Gonzalez *et al.*, 2003; Jin *et al.*, 2004).

3D inverse opal templates can be generated by colloidal crystal lithography (Sun *et al.*, 2004; Xia *et al.*, 2011; Li *et al.*, 2016), which are self-assembled templates created from spherical particles of a distinct size. The particles are often made out of SiO₂, polymethylmethacrylate (PMMA) or polystyrene (PS) and come in sizes from nanoscale to millimeter scale. The particles can be removed from the resulting template by wet etching or O₂-plasma. Composite inverse opal foams have been reported for instance for battery application (Li *et al.*, 2016).

Stereo- and multi-photon lithography can create freeform 3D templates in the micro- and mesoscale and is promising for 3D templates. For photonic MM, gold helices were studied and for mechanical MM, copper lattices were produced and investigated.

There are challenges to understand the deposition into such templates as laid out in Fig. 7. Some of these challenges have already been addressed for two-dimensional templates. The most important factor is the aspect ratio of a pore (Chen and Evans, 2004), if the aspect ratio is high, the deposition is limited via mass transfer into template, mainly migration and diffusion of ions (West *et al.*, 1998; West, 2000). A low aspect ratio, means the influence of the convection can be influencing the deposition which cannot be easily predetermined as the convection is heavily influenced by the shape of the template that is to be filled. Water-based electrolytes can create a significant amount of hydrogen evolution reaction and therefore, porosity and voids can be created during the filling. Pulse deposition is often used to improve electrodeposit quality and can be crucial to have the

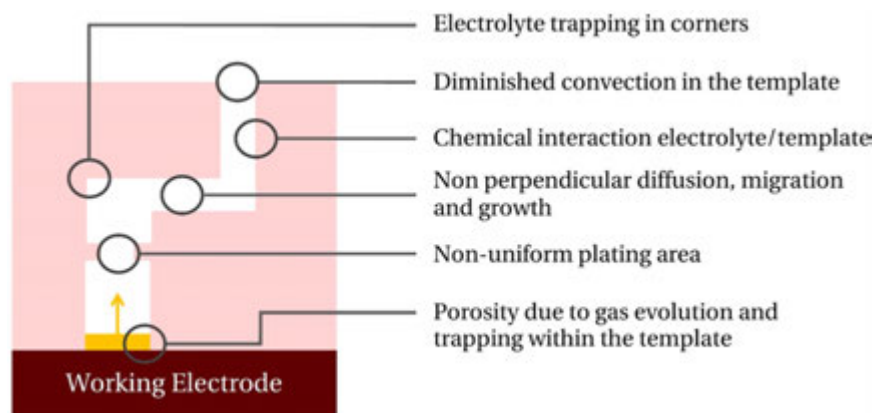


Fig. 7 Challenges of electrodeposition into complex 3D templates.

concentration of ions replenish during deposition pulses. Reverse pulse plating can be used to actively hinder and slow down the electrodeposition in the most accessible part of the template, increasing the filling ratio (Schurch *et al.*, 2018). Template-assisted electrodeposition shows promising results, see Fig. 5(d) and (e). It is an excellent technique for producing metal-based CMM in the future (Schürch *et al.*, 2020).

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Appendix A Supplementary Material

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.1016/B978-0-12-803581-8.11750-3>.

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3D and 4D Printing of Functional and Smart Composite Materials

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Introduction

Nowadays the application of 3D and 4D printing technologies for fabricating parts and devices is attracting much interest in many high technological sectors such as energy (Fu *et al.*, 2017; Li *et al.*, 2017), transport (Juechter *et al.*, 2018), biomedicine (Zuniga *et al.*, 2015), aerospace (Liu *et al.*, 2017) and aeronautics (Huang *et al.*, 2016). The interest is due to the possibility of manufacturing functional and smart 3D objects with complex shapes and high performance (Kokkinis *et al.*, 2015; Murr, 2016; Lee *et al.*, 2017; Tofail *et al.*, 2018; Li *et al.*, 2019). 3D printing shows several advantages in comparison to traditional fabrication techniques such as injection molding, CNC machining, sintering, plastic forming, or compaction, among others (Frazier, 2014; Lušić *et al.*, 2015; Murr, 2016; Lee *et al.*, 2017; Bandyopadhyay and Heer, 2018):

- Reduction in the geometrical restrictions imposed by classical fabrication techniques such as undercuts, draft angles and difficulties shown when accessing with machining tools to complicated areas in the fabricated part. This allows for designing and fabricating components with very complex geometries.
- Customization in the design of parts and devices allowing for a personalized fabrication. By traditional mass manufacturing techniques (e.g., injection molding), it is more difficult to add some personalization into the design of a product that is being fabricated, making rapid manufacturing (3D printing) a most suitable option for customized production.
- 3D printing allows for faster and cheaper fabrication of functional prototypes that can be tested in working conditions. This enables designers for identifying any potential flaws or weak points leading to a fast and low-cost verification, reparation, modification, optimization, and reproduction of the design.
- Elimination of expensive fabrication and post-processing equipment and tooling such as the molds used for manufacturing by injection molding.
- Reduction of material waste. By subtractive fabrication methods as CNC turning, milling or grinding the designed part is obtained by removing material from an initial piece. This originates a large volume of material that is wasted. 3D printing only uses the material that is necessary for fabricating the part as its working principle is the addition of material layer by layer until the 3D object is finished. This advantage makes 3D printing a more sustainable and environmentally friendly fabrication technology.
- Additive manufacturing technologies add the material only in the areas where it is necessary, then allowing for fabricating lighter parts and devices.
- The elimination of non-necessary equipment and tooling, together with the minimization of wasted material along fabrication leads to a considerable reduction in the fabrication process costs. Considering this, additive manufacturing is a very competitive technology for low volume of production.

Designing and fabricating employing composites is highly interesting due to the possibility of tuning their final physical properties (and, consequently, of the printed parts) according to the type and content of the materials combined along composite synthesis. In different sectors, such as high technological industries (electronics, transport, aerospace, among others) and construction, it is well-known the combination of different materials as composites for developing mechanical reinforced and lightweight structures, or giving to the material electrical, conductive, thermal, magnetic and optical properties (i.e., additional functionality) (Hanemann and Szabó, 2010; Nikzad *et al.*, 2011; Valentine *et al.*, 2017; Hassan *et al.*, 2018). In this sense, the development of functional materials, together with their incorporation in the fabrication by 3D printing, enables many possibilities in their application in sectors such as energy, transport, aerospace, aeronautics or biomedicine. On the other hand, when smart materials (also known as intelligent or responsive materials, and usually referred to as shape memory materials) are employed, 3D printing evolves to 4D printing, where the printed structures transform over time in a controlled manner due to an external stimuli (e.g., temperature, light, pH, electric or magnetic fields, stress or chemicals) (Ligon *et al.*, 2017). These materials and structures are of high importance in applications such as sensors, actuators or artificial muscles, as advanced composite printing allows for a higher degree of complexity and accuracy.

Composite Materials for Additive Manufacturing

The main materials used for additive manufacturing (AM) are: (1) polymers, divided into two groups: thermoplastics, such as polyamide (PA, nylon), acrylonitrile butadiene styrene (ABS), polyethylene (PE) or polylactic acid (PLA), and thermosets, most commonly known as resins (Ligon *et al.*, 2017); (2) metals (e.g., stainless steel, titanium, and aluminum alloys, among others) (Frazier, 2014; Tofail *et al.*, 2018); (3) ceramics (barium titanate –BaTiO₃–, alumina –Al₂O₃–, or zirconia –ZrO₂) (Kim *et al.*, 2018; Promakhov *et al.*, 2018); and (4) composites made by combining polymers, metals and ceramics (Fig. 1; Kokkinis *et al.*, 2015; Kalsoom *et al.*, 2016a; Parandoush and Lin, 2017; Gonzalez-Gutierrez *et al.*, 2018; Bekas *et al.*, 2019; Lengauer *et al.*, 2019).

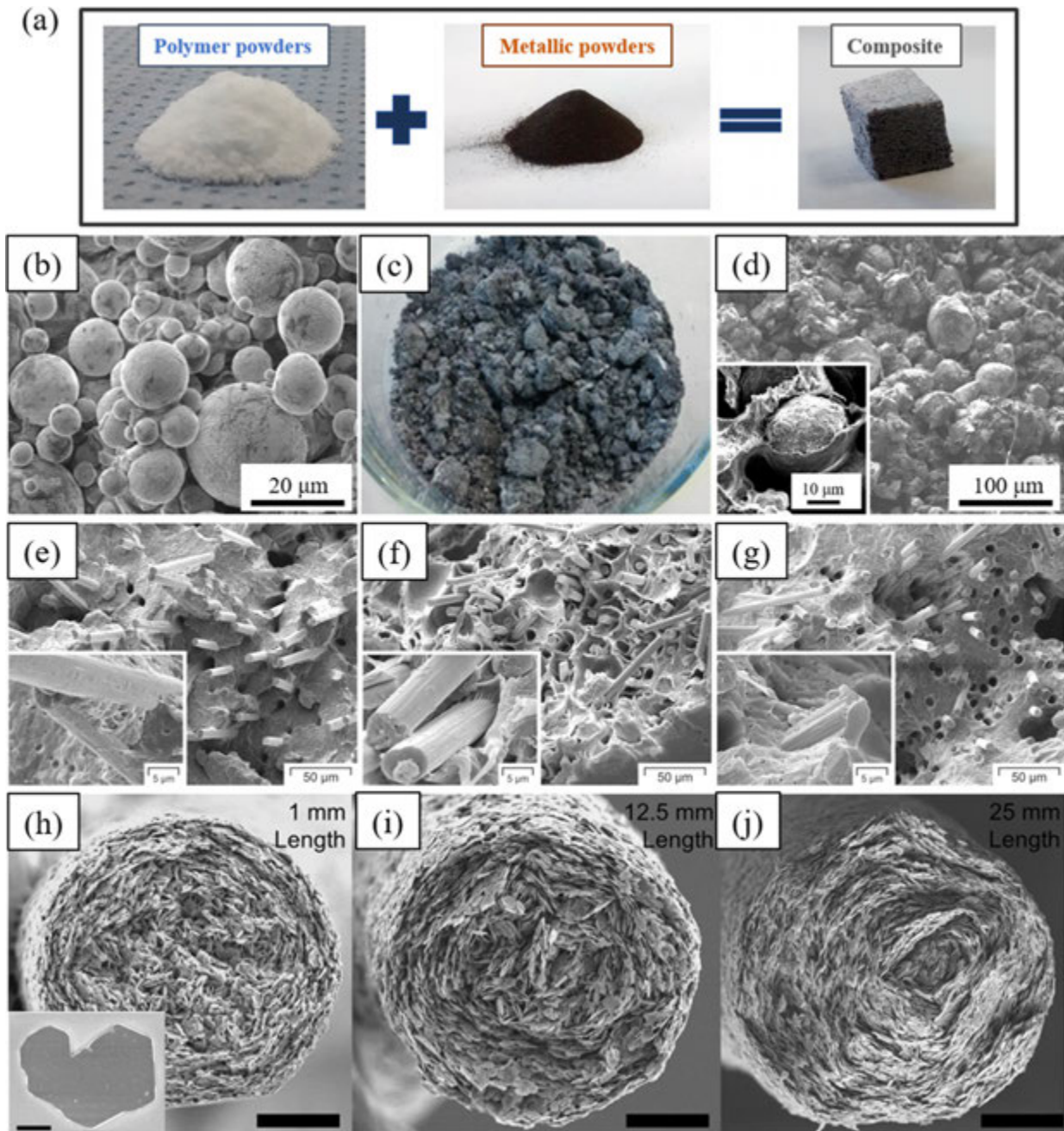


Fig. 1 (a) Starting polymer (polyethylene, PE), metallic particles (MnAlC), and synthesized composite (MnAlC-PE); (b) scanning electron microscopy (SEM) image of gas-atomized MnAl particles; (c) and (d) image and SEM image of MnAlC-PE composite. Inset in (d) shows a detail of a MnAlC particle embedded in polymer matrix. SEM images of cryo-fractured filaments made of composites of carbon fibers (CF) embedded in polypropylene (PP) matrix with different content of CF: (e) 10 vol%, (f) 15 vol%, and (g) 20 vol%. SEM images of filaments printed by robocasting using different nozzle lengths: (h) 1 mm, (i) 12.5 mm, and (j) 25 mm length. Scale bars 30 μm . Inset in (h) shows a SEM image of an alumina platelet. Scale bar 2 μm . Adapted from: (a) and (c) Palmero, E.M., Rial, J., de Vicente, J., *et al.*, 2018. Development of permanent magnet MnAlC/polymer composites and flexible filament for bonding and 3D-printing technologies. *Science and Technology of Advanced Materials* 19 (1), 465–473. (e)–(g) Spoerk, M., Savandaiah, C., Arbeiter, F., *et al.*, 2018. Anisotropic properties of oriented short carbon fibre filled polypropylene parts fabricated by extrusion-based additive manufacturing. *Composites Part A: Applied Science and Manufacturing* 113, 95–104. (h)–(j) Feilden, E., Ferraro, C., Zhang, Q., *et al.*, 2017. 3D printing bioinspired ceramic composites. *Scientific Reports* 7, 13759.

The use of composite materials in AM technologies allows for designing and fabricating objects with tuned properties by tailoring the combination of materials and their amount in the composite (Ligon *et al.*, 2017; Bekas *et al.*, 2019). In sectors such as construction and high technological industries (e.g., aeronautics, aerospace, or electronics) it is well-known the use of composites

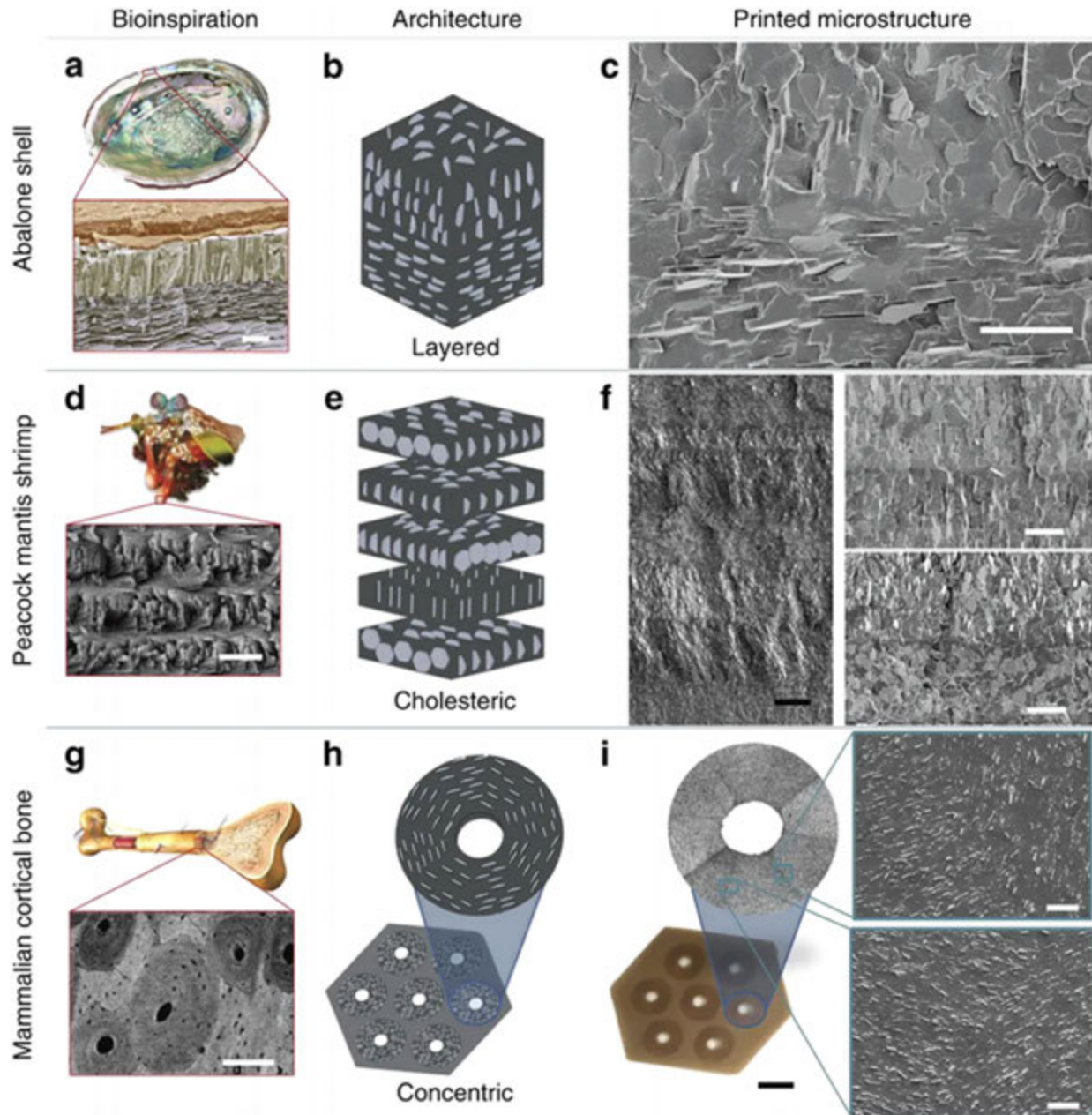


Fig. 2 Complex natural composites: (a) *Haliotidae* sp. abalone shell, (d) dactyl club of the peacock mantis shrimp and (g) mammalian cortical bone; together with their (b) layered, (e) cholesteric, and (h) concentric simplified structures, respectively. (c), (f) and (i) show SEM images of the composites obtained by 3D magnetic printing. Scale bars: 5 μm in (a); 25 μm in (c); 15 μm in (d); 50 μm and 20 μm for black and white in (f), respectively; 200 μm in (g); and 5 mm and 25 μm for black and white in (i), respectively. Reprinted from Martin, J.J., Fiore, B.E., Erb, R.M., 2015. Designing bioinspired composite reinforcement architectures via 3D magnetic printing. *Nature Communications* 6, 8641.

made of particles or fibers embedded in a matrix for obtaining different properties (Hanemann and Szabó, 2010; Nikzad *et al.*, 2011; Valentine *et al.*, 2017; Hassan *et al.*, 2018): electrical conductivity (Yang *et al.*, 2013; Grant *et al.*, 2015; Postiglione *et al.*, 2015), optical (Demir *et al.*, 2007; Pucci *et al.*, 2011; Mandel *et al.*, 2017), thermal conductivity (Burger *et al.*, 2016; Hu *et al.*, 2017; Kalsoom *et al.*, 2016b), and magnetic properties (Thévenot *et al.*, 2013; Jackson *et al.*, 2016; Palmero *et al.*, 2018). Additionally, composites are used for fabricating light-weighting parts in aerospace and aeronautics components for an increased fuel efficiency (Williams and Starke, 2003; Ghori *et al.*, 2018; Zhu *et al.*, 2018), and for enhancement of mechanical properties of structures (Delgado-Camacho *et al.*, 2018; Liu *et al.*, 2018; Rajak *et al.*, 2019), reinforcement that can be inspired in biological architectures that are found in the nature as the ones shown in Fig. 2 (Martin *et al.*, 2015).

The different materials used in AM usually are in filament, powder, resin or ink form, depending on the fabrication technique, that will be selected according to the starting material and the required properties of the final object (Nikzad *et al.*, 2011;

Hassan *et al.*, 2018; Tofail *et al.*, 2018; Bekas *et al.*, 2019). The fabrication of composites is performed by different techniques: (1) synthesis of composite pellets by solution casting, that are directly used for printing (Bellini *et al.*, 2005; Li *et al.*, 2016) or for extruding filaments to be employed as feeding material for the 3D-printers (Hwang *et al.*, 2015; Wei *et al.*, 2015; Palmero *et al.*, 2019a, 2020); (2) synthesis of inks by mixing the different materials (mixture of particles or fibers with hydrogels and polymers, followed by a dispersion process) (Sandoval and Wicker, 2006; Lewellyn-Jones *et al.*, 2016; Valentine *et al.*, 2017); or (3) mixture with a co-rotating twin-screw extruder (Dul *et al.*, 2018; Jiao *et al.*, 2019; Rimpongpisarn *et al.*, 2019).

Additive Manufacturing Technologies

AM is a bottom-up fabrication methodology that can be divided into different technologies according to the used materials, fabrication equipment and process. According to the standard EN ISO/ASTM 52900:2017, AM technologies are divided into seven categories: vat photopolymerization, powder bed fusion, material extrusion, material jetting, binder jetting, sheet lamination and directed energy deposition (Gonzalez-Gutierrez *et al.*, 2018; Tofail *et al.*, 2018).

Vat Photopolymerization

Photopolymerization consists in the selective solidification of a liquid photopolymer resin by a chemical reaction (curing) when it is exposed to light with a specific wavelength, e.g., X-rays, electron beam, ultraviolet (UV), and visible light (Gibson *et al.*, 2010). Despite these radiation sources have been used in research, UV is the most commonly employed, and focused light emitting diodes (LED) have shown up as an alternative source in the visible light spectrum (Gross *et al.*, 2017).

The technologies that employ this working principle are Stereolithography (SLA), Digital Light Processing (DLP), and Continuous Direct Light Processing (CDLP) (also known as Continuous Liquid Interface Production (CLIP)).

SLA technology utilizes a build platform which is submerged into a vat filled with liquid photopolymer resin. During the process a focused beam of UV light is projected onto the surface of the vat, mapping and selectively curing a layer of the design, followed by lifting up the platform. This process is repeated until the solid object is fabricated (Gross *et al.*, 2017; Torres-Sevilla, 2019). After 3D-printing, the object is in a green (i.e., not fully cured state), requiring a post-curing by UV light when high mechanical and thermal properties are needed (Torres-Sevilla, 2019).

In DLP technology, a digital light projector screen flashes a single image of each layer by a selectively masked light source along the complete surface of the platform at once (Fig. 3(a)) (Tesavibul *et al.*, 2012; Gonzalez *et al.*, 2017). After projecting the image, each layer of the object is formed by small bricks called voxels (corresponding to the pixels of the projected image). The voxel resolution (and in consequence the surface finish of the printed part) will be determined by the equipment, the resin and the printing parameters (Kuang *et al.*, 2019a). In comparison to SLA, DLP shows the advantage of a reduced printing time as each layer

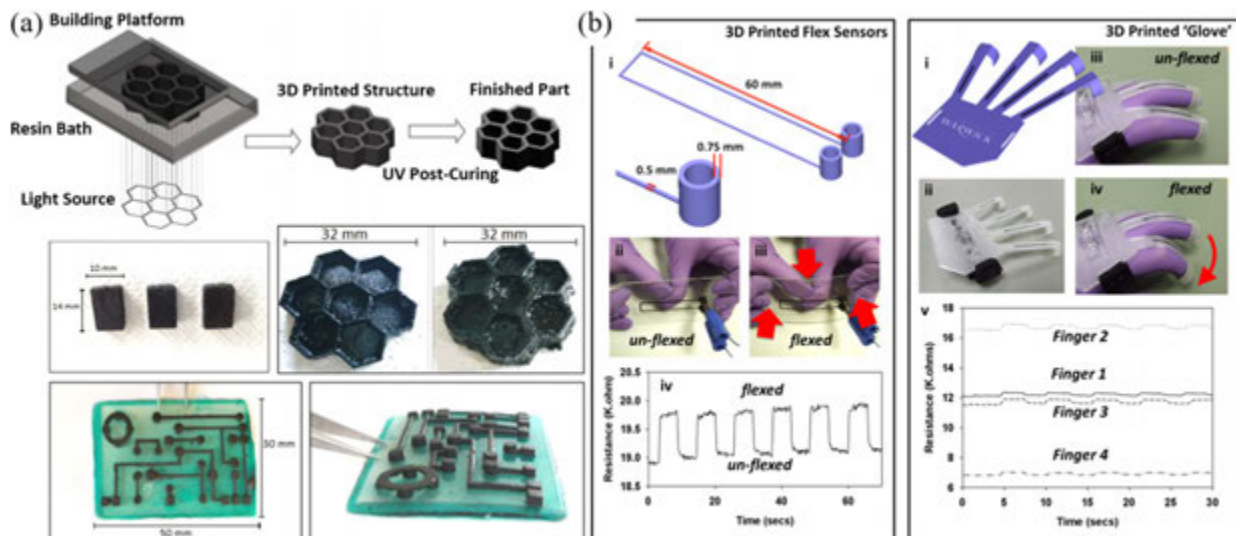


Fig. 3 (a) Scheme of the Digital Light Processing (DLP) technique (up), and 3D printed objects made of an acrylic photocurable resin containing carbon nanotubes (CNTs): cubes containing 0.3 wt% CNTs; hexagonal structures with an amount of 0.1 wt% and 0.3 wt% of CNTs (left and right, respectively); and circuit-like structure (0.1 wt%) (down). (b) 3D printed flex sensor: CAD design, printed sensor in un-flexed state and undergoing flexing, together with the resistance response while flexing (left); and 3D printed sensors able of generating a resistance response of each finger (right). Adapted from: (a) Gonzalez, G., Chiappone, A., Roppolo, I., *et al.*, 2017. Development of 3D printable formulations containing CNT with enhanced electrical properties. *Polymer* 109, 246–253. (b) Leigh, S.J., Bradley, R.J., Purcell, C.P., Billson, D.R., Hutchins, D.A., 2012. A simple, low-cost conductive composite material for 3D printing of electronic sensors. *PLoS One* 7 (11), e49365.

is exposed at once. The CDLP technology produces objects in the same manner as DLP, as the build platform is continuously moving upwards, allowing for faster printing times.

Photopolymerization allows for obtaining 3D-printed objects with complex shapes and a high spatial resolution, together with a smooth surface finish, which are provided by the spot size of the laser beam (Vaezi *et al.*, 2013; Ligon *et al.*, 2017). However, this technology shows some drawbacks as the lengthy post-processing needed to increase the mechanical performance of the printed objects, the limitation in materials available and the high cost of the equipment (Torres-Sevilla, 2019). Photopolymer resins (e.g., methacrylate-based as polymethyl methacrylate (PMMA), epoxy- and cationic- based resins) with different types of fillers (e.g., glass, carbon or ceramic fibers and particles) have been used for 3D printing parts made of multifunctional composites (Martin *et al.*, 2015; Gonzalez *et al.*, 2017; Feng *et al.*, 2019; Lantean *et al.*, 2019).

Binder Jetting

Binder jetting is an AM technology that selectively jets an adhesive material (binder agent) onto a layer of powder spread on the build platform. The 2D pattern for each layer is created by jetting the binding agent using an inkjet print-head. After binding each layer, the process is repeated by lowering the build platform until the object is completely printed (Ziaee and Crane, 2019). The printed piece usually will require a post-processing to improve their mechanical properties (Farzadi *et al.*, 2014; Gaytan *et al.*, 2015). The quality of the final object will be determined by the characteristics of the raw materials, powder bed formation, printing parameters, and post-processing (Ziaee and Crane, 2019). This is a fast method and does not require a powerful energy source, making it a low-cost technology. Moreover, with this technology the defects originated during heating are avoided, and it is compatible with a wide range of materials (Miyajima *et al.*, 2018; Ziaee and Crane, 2019). Binder jetting also allows manufacturing pieces made of composites for tuning their properties, such as strength or toughness (Christ *et al.*, 2015; Enrique *et al.*, 2018; Fonseca-Coelho *et al.*, 2019).

Material Jetting

Material jetting, also known as inkjet 3D printing, is based on the creation of objects by depositing droplets of liquid photopolymers through microscopic nozzles in a print-head (Fig. 4). After deposition, the droplets are cured and solidified using ultraviolet light (Yap *et al.*, 2017). In this technology, several printing parameters, such as printing orientation, object position, nozzle cleanliness and printing equipment preparation need to be considered and optimized (Tiberto *et al.*, 2013; Mueller *et al.*, 2015). Printing orientation is a critical parameter that will highly influence the dimensional accuracy and surface quality, as well as the final mechanical properties (Yap *et al.*, 2017).

There are two variations of this technology (Shen and Naguib, 2019): (1) Drop-On-Demand (DOD), where a heater or a piezoelectric transducer (to avoid the use of volatile solvents) applies heat to the ink originating a fast volume change within the ink reservoir and, consequently, causing the ink ejection through the nozzle (Martin *et al.*, 2008; Ligon *et al.*, 2017); and (2) Continuous Inkjet (CIJ), where a flowing jet is formed by pressure at the microscopic nozzle orifice, being broken into droplets by means of a disturbance generated by a vibrating piezoelectric. An electrostatic field is then generated to charge the droplets, being afterwards selectively deflected towards a target position on the receptor material (substrate). The undeflected droplets are collected in order to recycle and re-use them (Martin *et al.*, 2008).

Inkjet 3D printing has been widely used for producing functional objects: lightweight structures (You *et al.*, 2018), anatomical models (Yan *et al.*, 2018), smart wearable technology (Gao *et al.*, 2017), and biomedical scaffolds (Jakus *et al.*, 2015). Moreover, this technology has been recently applied for 4D printing (Shida *et al.*, 2017; Zhang *et al.*, 2019) and for the development of MEMS devices (Yang *et al.*, 2018) and structures with tuned properties (Eshkalak *et al.*, 2017; Xu *et al.*, 2018).

Material Extrusion

Material extrusion-based AM consist in depositing layer-by-layer molten and semi-molten materials onto a heated build platform through a nozzle attached to a printing head whose movement is controlled by a computer following CAD-defined layer contours. The materials dispensed through the nozzle may be polymers, pastes, polymer solutions and dispersions (Ligon *et al.*, 2017; Spoerk *et al.*, 2020). Moreover, it allows for printing composites where metallic and ceramic particles or fibers are embedded in a polymer or ceramic matrix, providing additional functionality to the printed objects (Ligon *et al.*, 2017; Bekas *et al.*, 2019). It includes several techniques such as Fused Filament Fabrication (FFF) – also known as Fused Deposition Modeling (FDM), trademarked by Stratasys –, 3D dispensing, 3D micro-extrusion, 3D fiber and micro-fiber deposition (also known as Robocasting (Deckers *et al.*, 2014)), 3D plotting (Ligon *et al.*, 2017) and Big Area Additive Manufacturing (BAAM) (Li *et al.*, 2016).

In FFF technology a polymer-based filament (Fig. 5(a)) feeds an extrusion print head which heats up the material allowing it to pass through a nozzle for dispensing the material onto the building surface (bed). In order to perform a successful 3D printing, several parameters need to be considered: extruding and bed temperature, nozzle design, build speed, and shape parameters such as layer height, fill density and pattern. Particular attention must be paid to the material rheology as it affects directly to the extrusion performance, both for the filament fabrication by extrusion and for 3D printing: a material with a non-suitable viscosity will originate fragile filaments (Palmero *et al.*, 2019a, Huber *et al.*, 2020) and difficulties during the printing process, e.g., clogging,

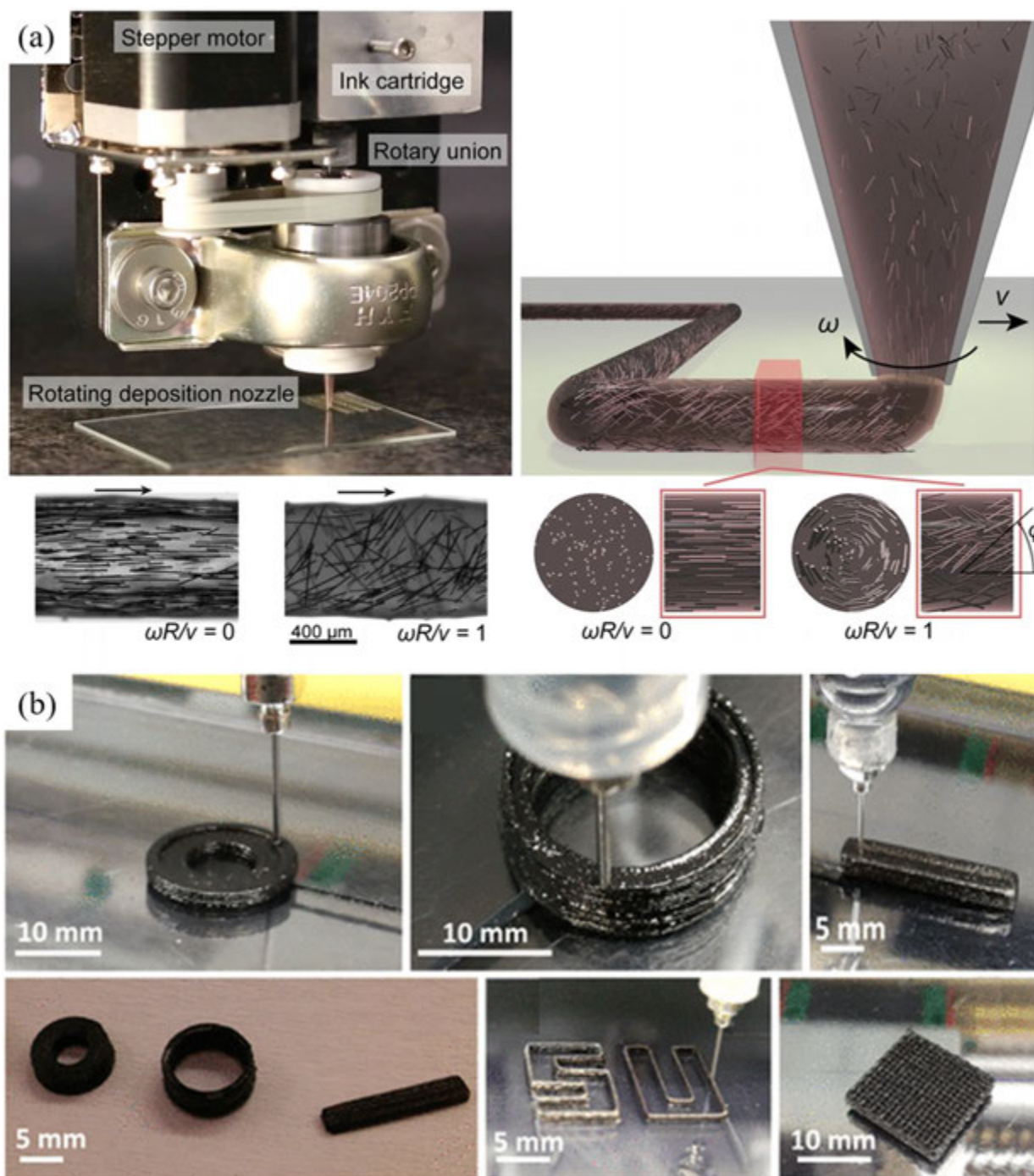


Fig. 4 (a) Device for rotational 3D printing (up left); scheme showing the fiber orientation during printing leading to a helical pattern (up right); optical micrographs of carbon fiber (1.3 wt%) filled epoxy filaments printed without rotation and with a high rotation (down left); and scheme of idealized fiber arrangement under the same rotation conditions (down right). (b) 3D printed magnetic cores, patterned letters and scaffold of highly loaded suspensions of iron oxide nanoparticles. Adapted from: (a) Raney, J.R., Compton, B.G., Mueller, J., *et al.*, 2018. Rotational 3D printing of damage-tolerant composites with programmable mechanics. *Proceedings of the National Academy of Sciences of the United States of America* 115 (6), 1198–1203. (b) Hodaie, A., Akhlaghi, O., Khani, N., *et al.*, 2018. Single additive enables 3D printing of highly loaded iron oxide suspensions. *ACS Applied Materials and Interfaces* 10 (11), 9873–9881.

discontinuous printing (Ligon *et al.*, 2017; Fallon *et al.*, 2019). Especially, in the case of filaments made of composite materials the rheology of the material will be highly influenced by the different materials that are combined in the composite and the amount of each of them (Palmero *et al.*, 2019b, 2020). The use of additives (stabilizers, dispersant agents or plasticizers) in the mixture is also being studied to improve the printed object quality and process efficiency.

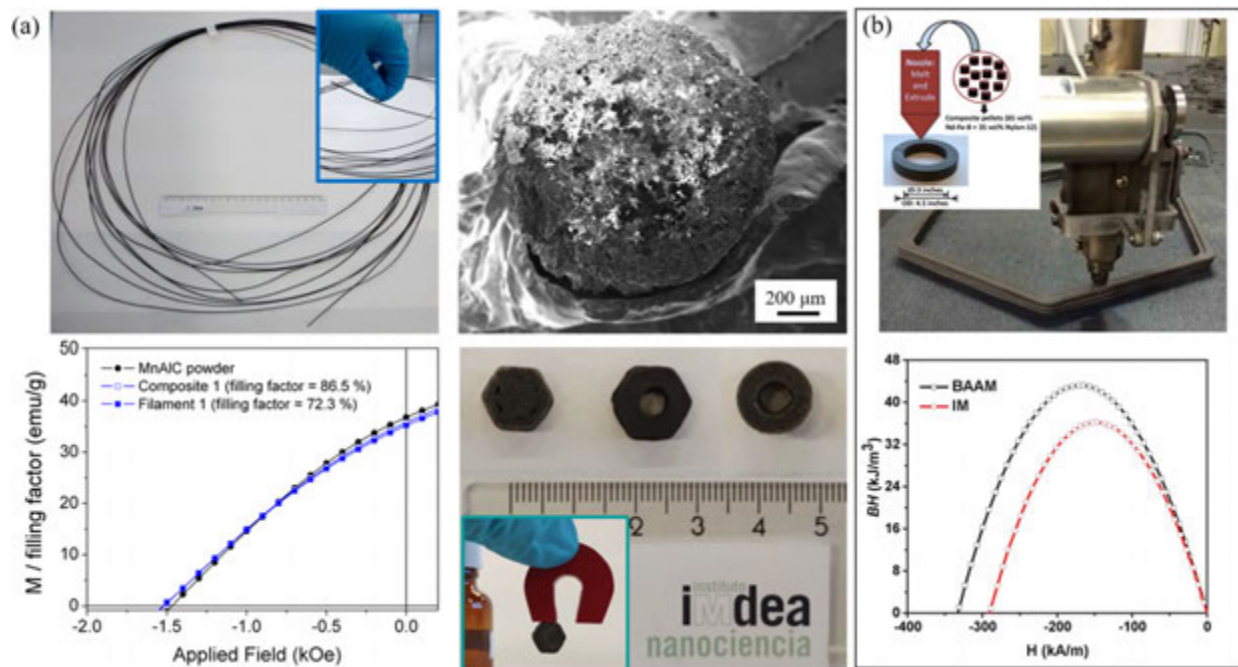


Fig. 5 (a) Extruded MnAlC/PE magnetic filament (a 20 cm ruler included for scale comparison) (up left); SEM image of the circular cross section of the extruded MnAlC/PE filament (up right); second quadrant of the hysteresis loops (with the magnetization, M , normalized to the filling factor) measured for MnAlC/PE composite, the corresponding extruded filament and the starting MnAlC powder (down left); 3D printed magnetic MnAlC-based pieces with different shapes by FFF. (b) Print nozzle depositing magnetic material with a specific shape (inset shows a scheme of melting and extrusion process of composite pellets made of NdFeB and nylon-12) (up), and room temperature maximum energy product $((BH)_{\max})$ of parts fabricated by BAAM, in comparison to parts produced by injection molding (down). Adapted from: (a) Palmero, E.M., Rial, J., de Vicente, J., *et al.*, 2018. Development of permanent magnet MnAlC/polymer composites and flexible filament for bonding and 3D-printing technologies. *Science and Technology of Advanced Materials* 19 (1), 465–473. (b) Li, L., Tirado, A., Nlebedim, I.C., *et al.*, 2016. Big area additive manufacturing of high performance bonded NdFeB magnets. *Scientific Reports* 6, 36212.

The most used polymers in FFF are ABS, PLA, polyamide (PA), polyethylene (PE), and polycarbonate (PC). Thermoplastics such as polyether ether ketone (PEEK) and polyetherimide (PEI) are also used due to their high mechanical and chemical resistance. Furthermore, fiber-reinforced and particles-filled filaments are attracting much interest nowadays because of the tuned properties that are achieved by the proper combination of materials with different properties (Hwang *et al.*, 2015; Wei *et al.*, 2015; Palmero *et al.*, 2019a, 2020).

3D dispensing, 3D micro-extrusion, 3D fiber and micro-fiber deposition and 3D plotting, due to their working principle, can be included in the category of 3D dispensing. This AM technology comprises different solidification methods: solidification by physical processes (e.g., crystallization and glass transition of thermoplastics, drying, coagulation...); through chemical reactions (e.g., cross-linking); and 3D printing of a polymer in a liquid media (Ligon *et al.*, 2017). Robocasting (which can be found in the literature also as Direct Ink Writing, DIW) is employed for the fabrication of dense ceramics and composites on the layer-wise direct extrusion of highly loaded colloidal slurry-based inks. This technology is useful for fabricating porous structures (catalyst supports, photonic crystals, or scaffolds for biomedical applications) and for advanced load bearing composites made by the infiltration of polymers, glasses and metals into those porous structures (Miranda *et al.*, 2006; Eqtesadi *et al.*, 2013).

Instead of requiring filament, BAAM technique combines materials melting, compounding for fabricating the composites (fiber and particles reinforced thermoplastic), and extrusion of the material (Fig. 5(b)) for a controlled deposition according to the CAD design (Li *et al.*, 2016).

AM techniques based on material extrusion show the advantages of using lower cost and easy to use equipment in comparison to other techniques, the broad range of materials available for printing, and the possibility of fabricating from small (e.g., 3D dispensing and FFF) to large pieces (e.g., BAAM). On the other hand, the 3D printed parts show a higher surface roughness, the accuracy and build speed may be lower, anisotropy of the mechanical properties of the printed objects needs to be considered, and supporting structures are required (Gonzalez-Gutierrez *et al.*, 2018).

Powder Bed Fusion

Powder Bed Fusion (PBF) technologies are based on the fabrication of an object by fusing the particles of a plastic, metal, ceramic powder into the desired shape using a thermal source (laser or electron beam) (Frazier, 2014; Wood, 2016; Datsiou *et al.*, 2019).

The technologies based on this method are Selective Laser Sintering (SLS), Selective Laser Melting (SLM), Direct Metal Laser Sintering (DMLS), Electron Beam Melting (EBM), and Multi Jet Fusion (MJF).

SLS technology consists in the production of a solid plastic object by sintering layers of powdered material. In this case, an initial layer of powder is spread on the build platform, and then the laser scans and sinters the cross section of the object, solidifying it (Tolochko *et al.*, 2000; Kumar, 2003). After that, the platform drops down and a new layer of powder is spread for the laser to solidify the next layer of the object (Frazier, 2014). This process is repeated until the solid three-dimensional object is fabricated. The printed objects present a certain level of porosity (potential weak points), that depends on the particle size distribution, material and process parameters (Flodberg *et al.*, 2018). In order to improve the mechanical strength, the green printed object is postprocessed by isostatic pressing, or resin infiltration (Stevinson *et al.*, 2006; Deckers *et al.*, 2012; Monzon *et al.*, 2015).

SLM and DMLS technologies employ a similar method to SLS for fabricating the object, however they are used for production of metal objects. The difference between SLM and DMLS is that by using SLM the powders are fully melted, while with DMLS the powders reach a temperature close to the melting point, favoring that the powders fuse together at a molecular level (Gardan, 2017). On the other hand, EBM technology uses a high energy beam for fusing the particles instead of a laser. In comparison to the other PBF technologies, the latter produces less residual stress in the manufactured objects, employs less energy and allows for faster printing rates. However, it shows lower quality of the surface finish and minimum feature size (Manfredi *et al.*, 2014). MJF technology is characterized by the use of two inks: fusing and detailing agent. In this case, the powder recoating method is the same as the used in SLS, and the fusing agent is jetted where it is necessary to melt the powders using an ink-jet print-head. The detailing agent is applied around the object edges to absorb heat, then reducing thermal bleeding and improving dimensional accuracy. After this, an infrared lamp is moved along the powder surface and the powders covered by the fusing agent melt (Sillani *et al.*, 2019). MJF technology allows for a high productivity due to the reduced manufacturing time and low cost per unit volume (Xu *et al.*, 2019; O'Connor and Dowling, 2020).

The most relevant advantage of PBF is that it is possible to manufacture complex objects and the availability of a wide range of powdered materials. However, these technologies employ more expensive equipment and use high cost powders (Karapatis *et al.*, 1999; Vock *et al.*, 2019). Another aspect that is necessary to consider is that particles with reduced size can be harmful and oxidized rapidly, being necessary a suitable handling and working conditions during fabrication (inert gas atmosphere within the chamber) (Ligon *et al.*, 2017; Tofail *et al.*, 2018; Gonzalez-Gutierrez *et al.*, 2018).

Despite PBF technologies are usually employed for fabricating plastic (PA, PEEK, or polyurethane – TPU), metal (aluminum, titanium, stainless steel and other alloys) or ceramic objects (Stevinson *et al.*, 2006; Liu *et al.*, 2017; Xu *et al.*, 2019; Datsiou *et al.*, 2019; Schönraht *et al.*, 2019), they also have been used for the fabrication of pieces made of composites (e.g., metal matrix with ceramic particles or carbon nanotubes, CNTs, as fillers) for enhancing their mechanical properties (Aversa *et al.*, 2017; Jiang *et al.*, 2019; Zhou *et al.*, 2018).

Sheet Lamination

Sheet lamination is an AM technology also known as Laminated Object Manufacturing (LOM). In this technology 3D objects are fabricated by cutting 2D cross-sections (sheets) using a laser or knives attached to the print head, being afterwards precisely bind using a localized energy source (hot rolling, ultrasounds – ultrasonic consolidation – or laser), chemical adhesives or brazing and welding. (Obikawa *et al.*, 1999; Park *et al.*, 2001). LOM allows for fabricating larger objects with a reduced cost together with a relatively higher building speed and supporting structures are not required (Ligon *et al.*, 2017). On the other hand, the fabrication of hollow structures is more difficult, and the manufactured objects may need a postprocessing for enhancing their dimensional accuracy and surface quality. LOM technology can be applied to different materials, such as metals, plastics, paper, ceramics, and composites (Klosterman *et al.*, 1998; Weisensel *et al.*, 2004; Parandoush and Lin, 2017). Furthermore, this technology has been used for manufacturing pieces made of thermoplastics such as PMMA and polycarbonate (PC) for biomedical applications (Sun *et al.*, 2010), and composites made of ceramic fibers embedded in a polymer matrix (Klosterman *et al.*, 1998; Weisensel *et al.*, 2004).

Directed Energy Deposition

Directed Energy Deposition (DED) allows for the creation of objects by melting the material (most frequently used for metals such as titanium, aluminum, stainless steel or copper) in powder or as a wire with a focused energy source as it is deposited by a nozzle on a surface (Ashish *et al.*, 2019). In a DED printer, the nozzle head moves around a fixed object for depositing the material in specific locations (Shamsaei *et al.*, 2015; Thompson *et al.*, 2015). Despite it is possible to build full parts with DED techniques, they are typically employed for repairing or adding additional material to existing objects. When combined with CNC machining in a single hybrid equipment, DED results in a powerful technology for obtaining a precise finish of the built part. DED also shows some drawbacks as the requirement of a large volume of inert gas when a fully inert chamber is needed; the necessity of post-processing for reaching the desired finish of the manufactured part; and the wasted material when not all the material sprayed by the nozzle is melted, reducing the efficiency of the technique (Zenou and Grainger, 2018).

Functional and Smart 3D and 4D Printed Composites

The versatility of 3D printing technologies in addition to the broad range of materials that can be used in the different AM methods allows for imparting added functionalities to the printed parts.

Composites With Magnetic Properties

Magnetic composites can be synthesized by embedding magnetic particles into a non-magnetic matrix, that will be selected according to the technology used for fabricating the printed magnetic parts (e.g., polymer matrix, curable hydrogel or solvent). The magnetic properties of the printed parts will depend on the properties of the starting particles, the composite synthesis, the design of the object and the 3D printing processing.

3D printing has been used for the fabrication of magnetic cores with diverse geometries using highly loaded suspensions of iron oxide nanoparticles (Fig. 4(b); Hodaei *et al.*, 2018). The stability, viscosity and viscoelastic properties of highly loaded suspensions with an optimized content of additives was studied, as it is an important factor to consider in order to obtain an adequate printing process ensuring the homogeneity of the printed part.

Magnetite (Fe_3O_4) nanoparticles have been also employed to print functional objects. Tiberto *et al.* (2013) studied the aggregation effects due to interactions between nanoparticles when 3D printing films using magnetic inks based on magnetite nanoparticles of different sizes. It was determined that the ejection process during ink printing influences the degree of aggregation between particles and would allow for modulating the magnetic response of the printed film. Furthermore, Fe_3O_4 nanoparticles have been demonstrated to work as suitable fillers in composites for fabricating magneto-responsive object with complex designs by DLP (Lantean *et al.*, 2019). In this work, authors tuned the mechanical properties and magnetic response of the printed objects by tailoring their geometry and nanoparticles content to perform magnetic-controlled movements (rolling, stretching, or folding/unfolding), with potential applications in soft robotics, flexible electronics or biomedicine.

In the permanent magnet (PM) sector, there is an increasing interest on developing components and devices by 3D printing a broad range of PM materials due to the advantages of this technology. MnAl alloy is a promising rare earth-free alternative PM material provided obtaining its ferromagnetic phase (τ -phase) in addition to a successful development of its PM properties, such as coercivity enhancement (Rial *et al.*, 2018). Palmero *et al.* (2018) demonstrated the possibility of obtaining magnetic filaments for printing by FFF (Fig. 5(a)) based on gas-atomized MnAlC particles embedded in a polymer matrix (Fig. 1(a)–(d)). It was demonstrated that the methods used for composite synthesis and filament extrusion do not deteriorate the magnetic properties of the particles. Size distribution of the particles in the composite is a key factor that can be tuned for obtaining continuous and flexible filaments with an increased particle content suitable for printing objects by FFF (Palmero *et al.*, 2020). Compounds based on another rare earth-free PM alternative materials such as strontium ferrite ($\text{SrFe}_{12}\text{O}_{19}$) using different polymer matrices (e.g., ethylene ethyl acrylate (EEA) copolymer, or polyamide PA12) have been analyzed: Huber *et al.* (2020) studied the effect of the filling fraction of the composite on its processability for obtaining adequate filaments for printing. In this work the magnetic performance of the printed pieces was analyzed both with and without an externally applied magnetic field during printing (the remanence of the printed pieces without alignment field was around 40% lower, showing an anisotropic behavior); Palmero *et al.* (2019b) analyzed the influence of particle size on extruding continuous and flexible filaments studying two different PM materials with well-differentiated particle sizes: $\text{SrFe}_{12}\text{O}_{19}$ and NdFeB particles with a mean particle size of 5 μm and 50 μm , respectively. Authors observed that reduced particle size enabled the production of flexible filaments with an increased PM particle content (over 90 wt%). NdFeB-based composites for 3D printing are being deeply studied (Huber *et al.*, 2016, 2017), even for producing 3D printed magnets at a large scale. Li *et al.* (2016) fabricated isotropic near-net-shape NdFeB bonded magnets by BAAM and using as starting material composite pellets based on isotropic NdFeB powders embedded in PA12. The magnetic and mechanical properties were studied and compared to those of injection molded magnets, showing comparable or even better performance (Fig. 5(b)).

Composites With Tuned Thermal Properties

Controlling the fiber orientation inside a composite allows for enhancing the thermal conductivity of 3D printed parts. Spoerk *et al.* (2018) demonstrated that for composites made of short carbon fibers embedded in a polypropylene (PP) matrix (Fig. 1(e)–(g)) by tailoring the printing orientation in FFF, different mechanical and thermal properties can be obtained. A strong anisotropy was observed for properties such as flexural and impact resistance, as well as thermal conductivity, property that was three times higher along the printing (and fiber) direction than for the perpendicular direction (Fig. 6(a)).

Nikzad *et al.* (2011) developed composites based on metallic (iron and copper) particles embedded in a polymer matrix of ABS to be used for rapid prototyping by FFF. The composites had a particles content of up to 40 vol%. By adding a particular %vol of iron particles, the thermal conductivity of the composite increases by approximately the same percentage. Using composites with an enhanced thermal conductivity for printing parts by FFF will originate more thermally stable parts and, consequently, more dimensionally accurate.

The work performed by Hu *et al.* (2017) reported a method for improving the thermal conductivity based on the synthesis of composites made of epoxy resin containing ordered 3D boron nitride network by combining ice-templating self-assembly and

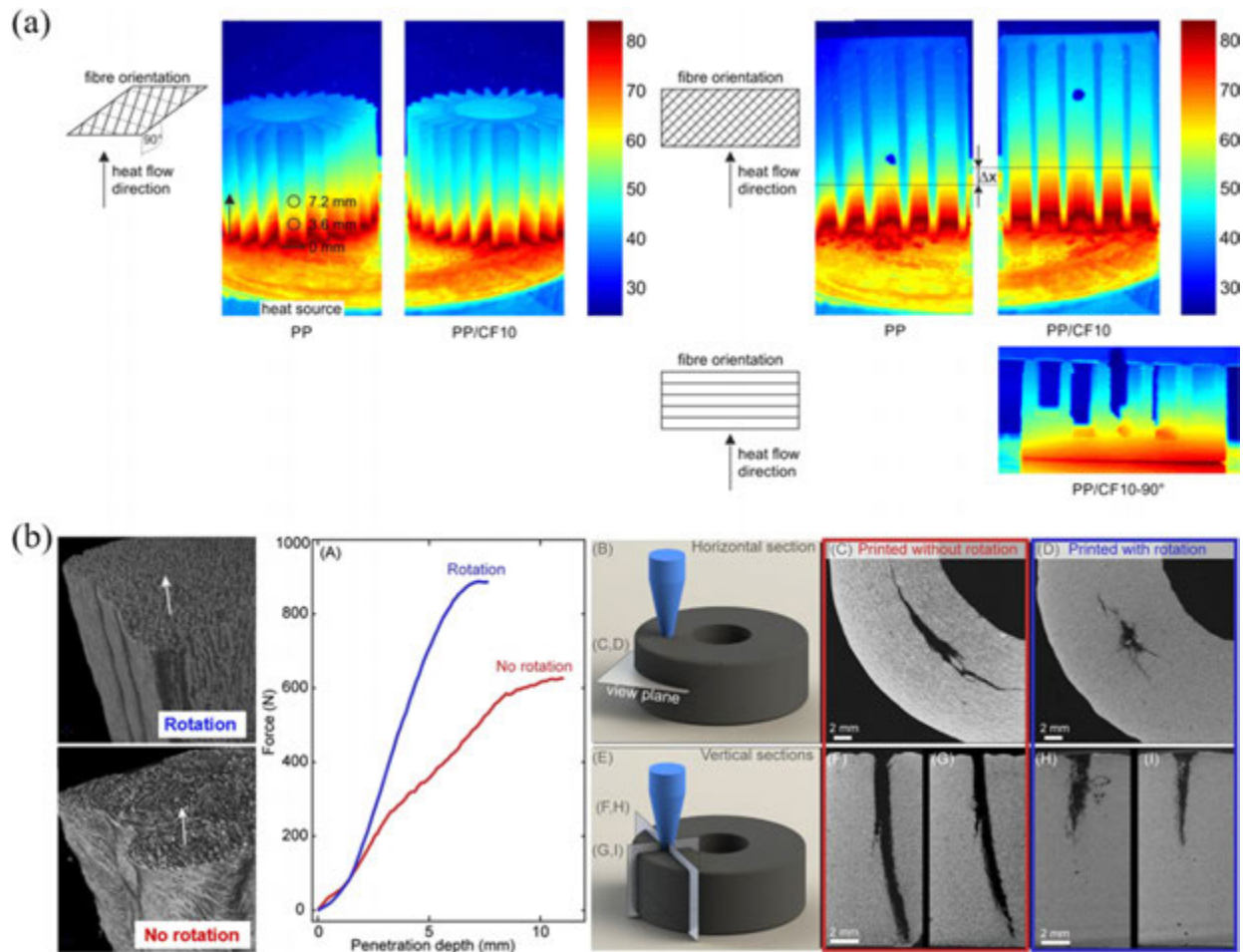


Fig. 6 (a) Infrared tomography measured for 3D printed parts made of polypropylene (PP) and composite based on PP containing 10 vol% of carbon fibers. A sketch showing the heat flow direction with respect to the fiber orientation is plotted in the left side of each tomography. (b) X-ray micro-tomographies showing the cross sectional views of the internal structure of carbon fiber and epoxy composites printed with and without rotation (white arrow indicates print direction) (left); results of the puncture loading experiments performed on the printed samples and images of the top surface and cross sectional views of the planes indicated in the schemes (right). Adapted from: (a) Spoerk, M., Savandaiah, C., Arbeiter, F., *et al.*, 2018. Anisotropic properties of oriented short carbon fibre filled polypropylene parts fabricated by extrusion-based additive manufacturing. *Composites Part A: Applied Science and Manufacturing* 113, 95–104. (b) Raney, J.R., Compton, B.G., Mueller, J., *et al.*, 2018. Rotational 3D printing of damage-tolerant composites with programmable mechanics. *PNAS* 115 (6), 1198–1203.

infiltration techniques. The polymer composites exhibit a higher thermal conductivity at a filling fraction of 34 vol% than that of composites with random distribution. The reported results show potential for application of these composites in the fabrication of thermal interface materials for electronic packaging and 3D integrated circuits as well as their inclusion in aerospace materials when a high heat dissipation is required.

Composites for Reinforced Architectures

The use of composites based on fibers embedded in a matrix is commonly used in different sectors such as construction, aerospace or aeronautics for obtaining structures with enhanced mechanical properties. There are several works that being inspired by composites found in nature have translated these complex architectures to the development of reinforced structures.

Feilden *et al.* (2017) reported the use of robocasting to print scaffolds made of composites based on ceramics obtaining microstructures unachievable by other fabrication techniques. Cross section SEM images of the filaments used in robocasting are shown in Fig. 1(h)–(j) demonstrating that the nozzle diameter has a strong effect on the alignment of the alumina platelets. The complex shapes and structures, with enhanced mechanical properties such as toughness, were achieved by controlling the velocity gradients during printing and the rheology of the composites containing high loading of anisotropic platelets. This study shows how the combination of 3D printing and microstructure control offers new possibilities in the design and fabrication of materials with controlled fracture, enhanced toughness, high specific strength and defect tolerance.

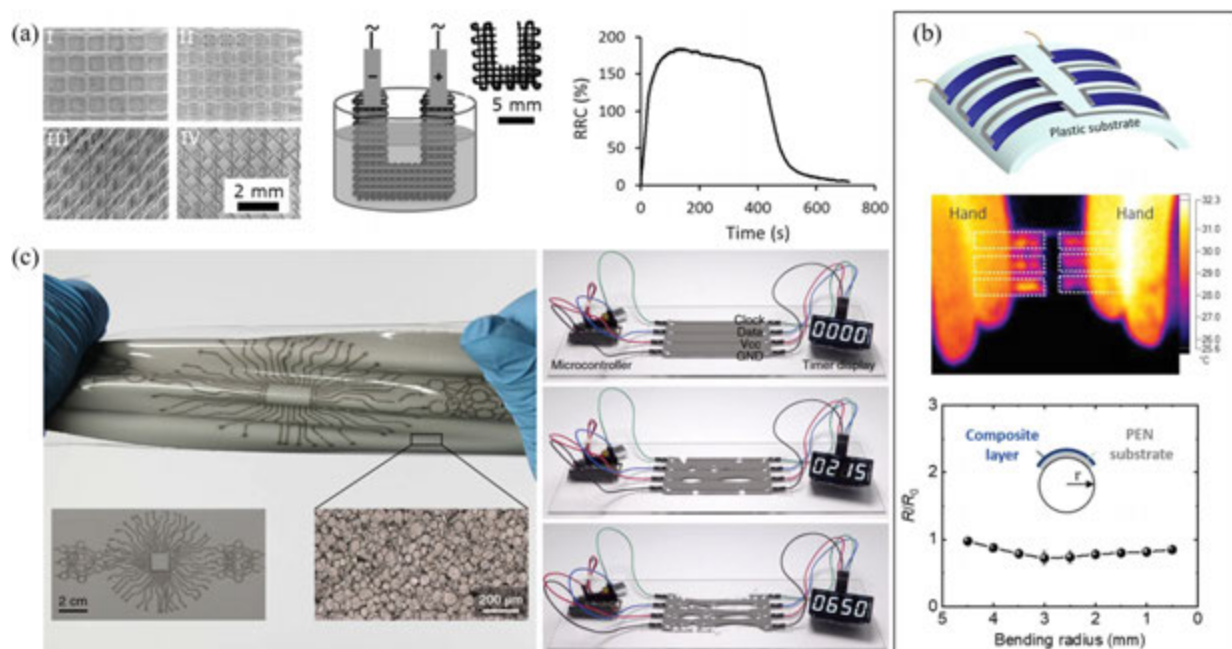


Fig. 7 (a) Conductive scaffold structures made of nanocomposites (carbon nanotubes/PLA): Top view SEM images of 3D printed scaffolds with different patterns (left); and scheme of the liquid sensitivity test performed using a printed and U-shaped cut scaffold, together with the variation of the relative resistance change (RRC) of a liquid sensor during the immersion/drying cycles. (b) Scheme showing the structure a 3D printed flexible thermoelectric generator (TEG) (up); infrared thermal image of the TEG with finger touch; and graph plotting the resistance changes vs. bending radius of the composite film on plastic surface (down). (c) Stretched and twisted composite based on liquid metal (LM) EGaIn alloy microdroplets suspended in silicone. The lower left image shows the intricate design of electrically conductive traces of the undeformed sample, close to an optical micrograph of the LM microdroplets in the elastomer at 50 vol%. Images in the right side show representative examples of reconfigurable material (LM loading of 50 vol%) transmitting DC power and digital signals. Adapted from: (a) Chizari, K., Daoud, M.A., Ravindran, A.R., Theriault, D., 2016. 3D printing of highly conductive nanocomposites for the functional optimization of liquid sensors. *Small* 12 (44), 6076–6082. (b) Kee, S., Haque, M.A., Corzo, D., Alshareef, H.N., Baran, D., 2019. Self-healing and stretchable 3D-printed organic thermoelectrics. *Advanced Functional Materials* 29 (51), 1905426. (c) Markvicka, E.J., Bartlett, M.D., Huang, X., Majidi, C., 2018. An autonomously electrically self-healing liquid metal – elastomer composite for robust soft-matter robotics and electronics. *Nature Materials* 17, 618–624.

In the nature, fiber composites are abundant, and they present a wide range of structures where reinforcing particles are organized into complex architectures leading to enhanced mechanical properties. Fig. 2(a), (d), and (g) show some examples that can be found in the natural world including the abalones shells, the dactyl clubs of peacock mantis shrimp and a mammalian cortical bone (Martin *et al.*, 2015). Martin *et al.* (2015) reported a 3D magnetic printing approach which combines real-time colloidal assembly with 3D printing to develop highly programmable discontinuous fiber-based composites. SEM images of the 3D printed microstructures emulating the architectures found in nature are shown in Fig. 2(c), (f), and (i), demonstrating the high customization level when designing and fabricating fiber-based composites with arbitrary geometries.

Raney *et al.* (2018) developed a rotational 3D printing method that allows for controlling the carbon fiber orientation in an epoxy matrix when printing by varying the nozzle rotation speed relative to the printing speed (Fig. 4(a)). By applying this printing method, it is possible to obtain composites with defined fiber arrangements, microstructural complexity, increased mechanical performance and enhanced damage tolerance (Fig. 6(b)). Authors stated the possibility of fabricating parts with programmed strain and failure distribution by designing adjacent regions with different mechanical properties, as well as the possibility of broaden this technology to its use for other anisotropic fillers combined with different matrix materials, enabling designed electrical, thermal, or optical properties.

Electrically Conductive Composites for Electronics and Sensing Devices

Electrically conductive composites can be obtained by the method reported by Chizari *et al.* (2016) where scaffolds were fabricated by solvent-cast 3D printing of composites made of carbon nanotubes (CNTs) embedded in a PLA matrix for their use as liquid sensors (Fig. 7(a)). Authors analyzed the influence of printing parameters (filament diameter, printing pattern or scaffold thickness) on the sensor sensitivity. By reaching an amount of 30 wt% of CNTs in the composite the relative resistance change (RRC) of the liquid sensor is about 78% applying a low voltage of 1.5 V. These highly conductive structures could be applied in the fabrication of complex structures to be used for electronics in 3D circuits (e.g., conductive interconnections, resistances or capacitors) and as gas or strain sensors.

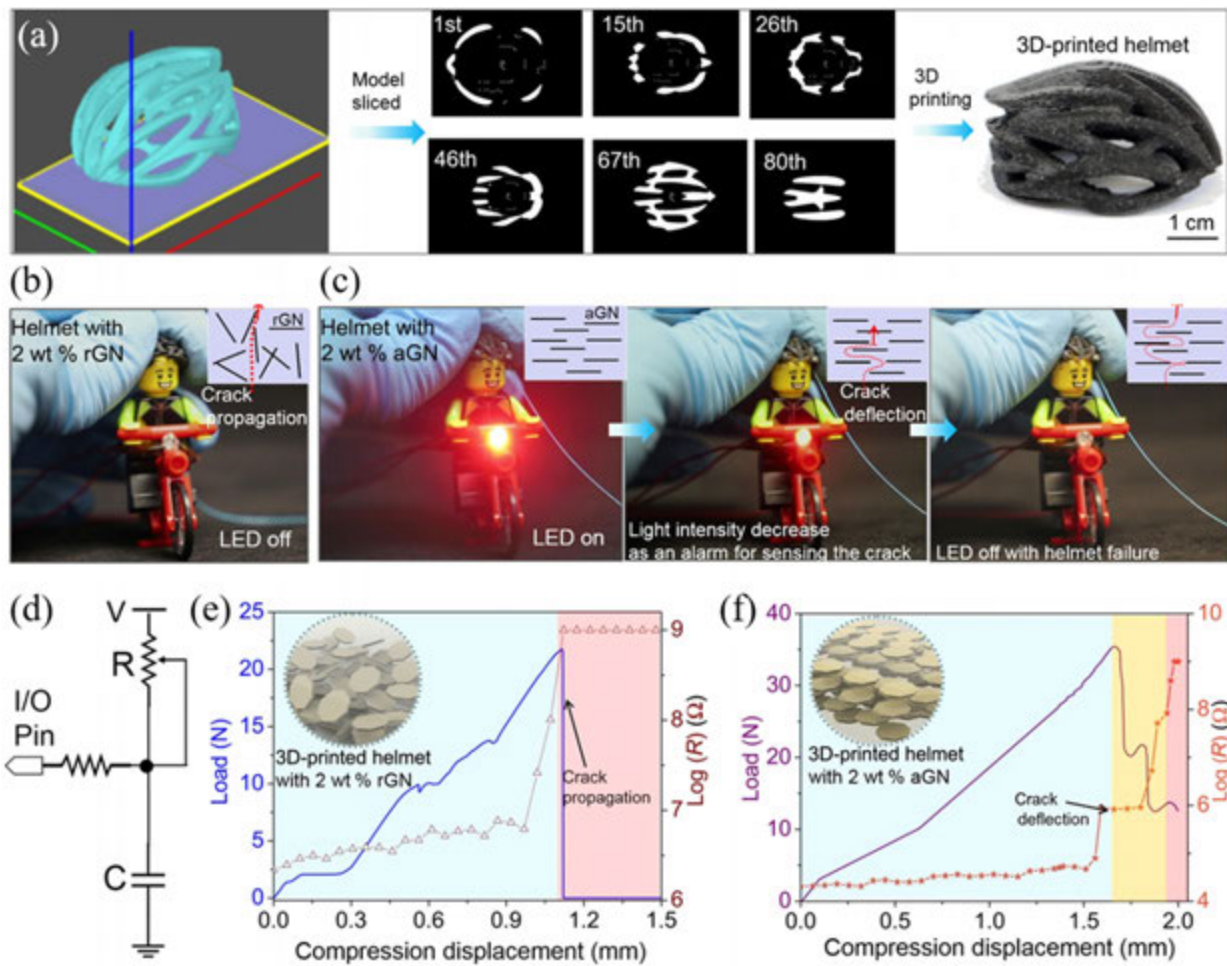


Fig. 8 (a) 3D printing process of a self-sensing smart helmet, from design to electrically assisted 3D printing by SLA and made of a nanocomposite consisting in graphene nanoplatelets embedded in a photocurable resin. Demonstration of the self-sensing properties of the 3D printed helmets using (b) random GNs (rGNs) and (c) aligned GNs (aGNs). (d) Electric circuit employed for testing the 3D printed helmets. Graph showing the compression force of the printed helmet vs. compression displacements and the change in the resistance for helmets based on (e) rGNs and (f) aGNs. Adapted from Yang, Y., Li, X., Chu, M., *et al.*, 2019. Electrically assisted 3D printing of nacre-inspired structures with self-sensing capability. *Science Advances* 5 (4), eaau9490.

CNTs were also used in the work reported by Gonzalez *et al.* (2017) (Fig. 3(a)). In this case, CNTs were added to an acrylic photocurable based formulation, whose viscosity was optimized to obtain the best composition suitable for printing. 3D printed structures were fabricated by DLP with a content of up to 0.5 wt% of CNTs, obtaining an increased conductivity in comparison to the neat matrix proportional to the amount of CNTs.

Yang *et al.* (2019) reported the fabrication of complex structures by electrically assisted 3D printing. Graphene nanoplatelets (GNs) are aligned by an electric field along 3D printing within the polymer matrix. The obtained structure with 2 wt% of GNs shows lightweight property and specific toughness and strength comparable to natural nacre. As observed in Fig. 8, the 3D printed smart helmet with aligned GNs is able of sensing its damage by means of a resistance change. This type of bioinspired structures combining both mechanical performance and electrical self-sensing capabilities show potential applications in biomedicine, aerospace or sports armors.

Leigh *et al.* (2012) developed conductive thermoplastic composites to print electronic sensors able to detect mechanical flexing (as the shown in Fig. 3(b) where the flexing movements of the fingers can be sensed through the resistance response generated by the printed sensors placed onto each finger) and capacitance changes. Authors used conductive carbon black fillers in a formulation of polycaprolactone for printing the sensors by FFF method.

In close relation to the property of being electrically conductive, the development of self-healing devices appears as an attractive option for the development of flexible and wearable electronics and sensors. Consequently, there is an increasing need of developing energy-harvesting solutions with high deformability and self-healability and compatible with those wearable devices allowing them for being self-powered. Kee *et al.* (2019) demonstrated the possibility of 3D printing a self-healing and stretchable thermoelectric generator (TEG) (see Fig. 7(b)). The composite exhibited a viscoelastic behavior and a stretchability up to 35%

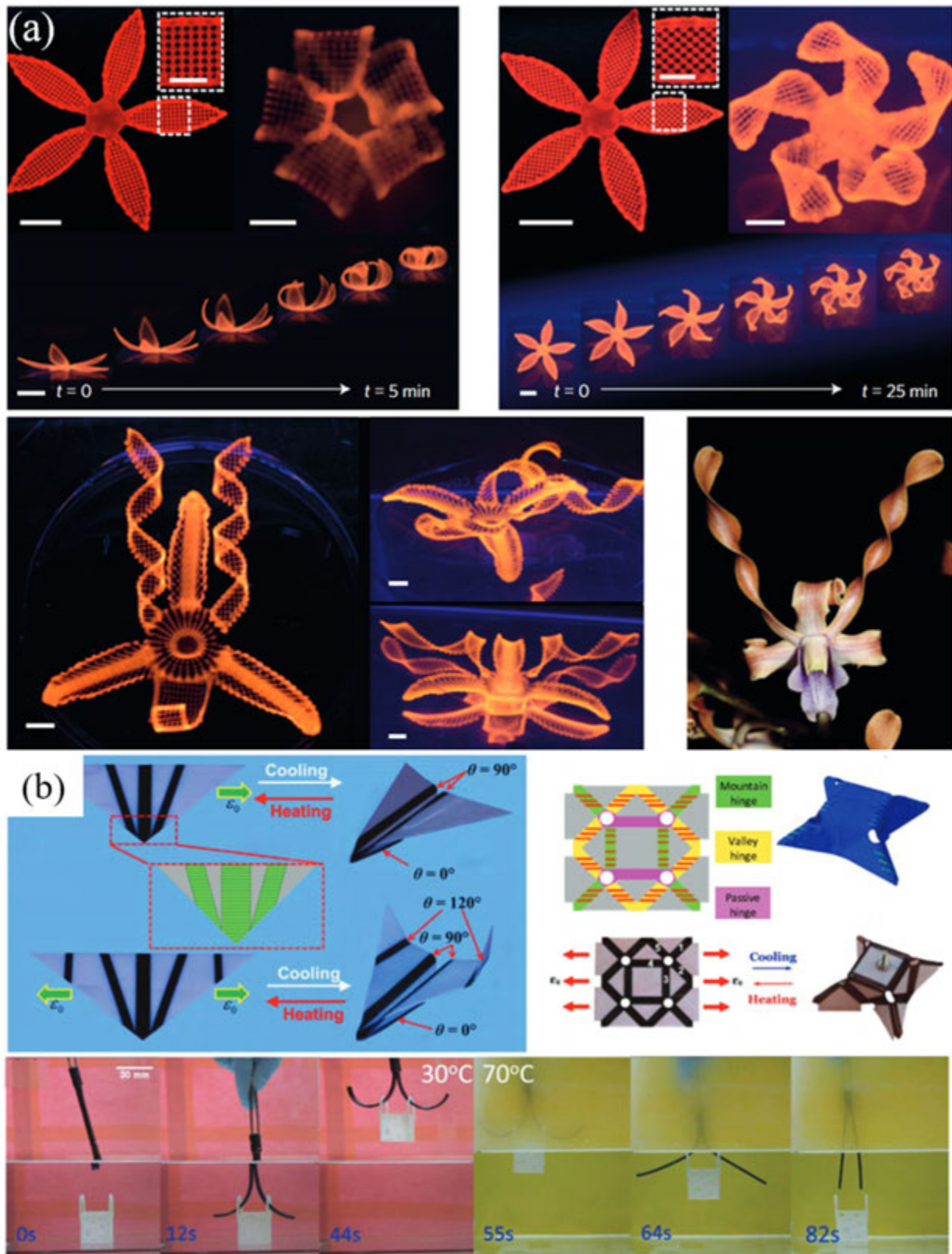


Fig. 9 4D printing of complex and smart structures. (a) Simple flower obtained by ink printing of cellulose fibrils in hydrogel which change their morphology by swelling when immersing in water. Scale bars, 5 mm (up); and swollen structure of a complex flower inspired by the *Dendrobium helix* orchid. Scale bars, 5 mm (down). (b) Self-folding airplane and table made of shape memory polymers (SMP): sheet with strategically located hinges allowing for bending specific part to form the desired shapes (up); and smart hook made of 3D printed composite strips connected at the end, that bends and gets straight again under water at specific temperature (down). Adapted from: (a) Gladman, A.S., Matsumoto, E.A., Nuzzo, R.G., Mahadevan, L., Lewis, J.A., 2016. Biomimetic 4D printing. *Nature Materials* 15, 413–418. (b) Kuang, X., Roach, D.J., Wu, J., *et al.*, 2019b. Advances in 4D printing: Materials and applications. *Advanced Functional Materials* 29 (12), 1805290.

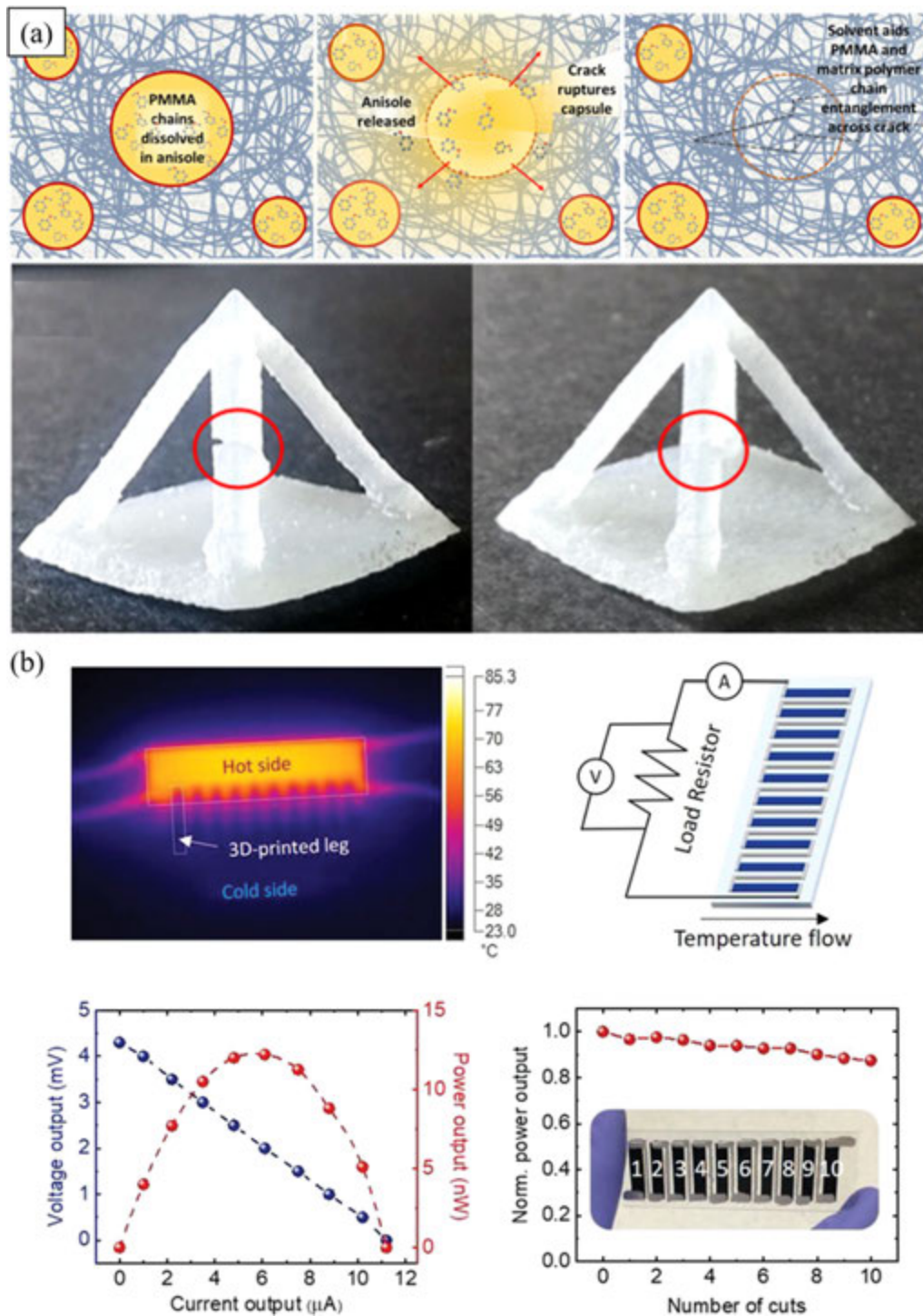


Fig. 10 Self-healing structures. (a) Schematic illustration (up) of the composite where the microcapsules containing PMMA dissolved in anisole are surrounded by the polymer. When a crack propagates, the microcapsule breaks, and the encapsulated solvent diffuses into the polymer, allowing for the polymer chain entanglement, i.e., healing the crack. Images of stereolithographic 3D printed parts (down) containing 5 wt% anisole with PMMA capsules where the fracture and the healed section are highlighted in red circles. (b) Infrared image of a 3D printed flexible thermoelectric generator (TEG) showing its thermal gradient (up left); to analyze the power generation performance of the printed TEG, the current and voltage were measured by a variable load resistor (down left); and the normalized power output with respect to the number of cuts of 3D printed legs. Adapted from: (a) Sanders, P., Young, A.J., Qin, Y., *et al.*, 2019. Stereolithographic 3D printing of extrinsically self-healing composites. *Scientific Reports* 9, 388. (b) Kee, S., Haque, M.A., Corzo, D., Alshareef, H.N., Baran, D., 2019. Self-healing and stretchable 3D-printed organic thermoelectrics. *Advanced Functional Materials* 29 (51), 1905426.

strain and self-healing properties with a fast response time (1 s), characteristics that lead to the composite to maintain the thermoelectric properties during stretching and fracturing. The 3D printed TEG retained more than 85% of its initial power output after repetitive cutting and operating at human body temperature.

Another example of self-healing flexible interconnected circuit is the one reported by Markvicka *et al.* (2018) where the composite is made of liquid metal (LM) droplets (EGaIn alloy, eutectic gallium-indium) suspended in a soft elastomer (silicone). In the deposited system, when damaged by stretching, as shown in Fig. 7(c), the LM droplets break and form new connections with adjacent LM for re-routing the electrical signal, making it a robust electronic system as demonstrated by the self-repairing digital counter shown in the figure that is able to continue working after a considerable mechanical damage. The proposed development shows up as a promising candidate to be implemented in diverse applications (e.g., wearable electronics).

4D Printing of Smart Composites

3D printed objects typically retain the shape and properties along their lifetime. However, the fabrication of 3D printed smart structures, that are able of changing their shape and properties in a controlled manner according to external stimuli (e.g., temperature, pH, light, water, electromagnetic radiation) leads to 4D printing (considering the time as the fourth dimension) (Ligon *et al.*, 2017).

Gladman *et al.* (2016) reported the 4D printing of composite architectures made of cellulose fibrils embedded in hydrogel. The printed structures, inspired in botanical systems as shown in Fig. 9(a), were fabricated by ink printing. The localized anisotropic swelling behavior of the architectures when immersing in water was controlled by alignment of cellulose fibrils along designed 4D printing pathways. This 4D printing method benefits from a proper combination of materials and geometry allowing for controlling the structures in space and time. This method could be extended to other materials such as liquid-crystal elastomers and anisotropic metallic fillers. This study presents new opportunities in biomedicine (tissue engineering and biomedical devices) as well as soft robotics sectors.

4D printing using composites based on shape memory polymers (SMP) allows for creating complex 3D architectures (Kuang *et al.*, 2019b). Fig. 9(b) shows how smart and strategically located hinges printed on a sheet enable active origami. They permit a programmable self-folding process obtaining 3D complex structures (e.g., airplane or table) (Ge *et al.*, 2014; Yuan *et al.*, 2017). Another example of a printed object that reacts with the change in the temperature is shown in Fig. 9(b). A printed hook made of SMP after one-step programming will bend and keep that shape at 30°C to lift a small box immersed in a liquid. After increasing the temperature up to 70°C, the arms will get straight again, dropping the box (Wu *et al.*, 2016).

Self-healing property (Fig. 10) is not only interesting for electrically conductive 3D printed systems (Figs. 7(b) and 10(b)), but also for repairing other structural designs made of different materials without the necessity of an external agent. Fig. 10(a) shows a 3D printed structure made of a photocurable resin containing 5 wt% anisole with PMMA capsules fabricated by SLA (Sanders *et al.*, 2019). After performing a cut in the piece, the fracture planes were pushed back together and permitted to heal for three days at 25°C. The self-healing mechanism based on solvent welding process is schematically shown in the figure. The work states that the solvent welding process allows for recovery 87% of the initial critical toughness. The results from this work are promising for applications such as personalized medicine. Furthermore, additional functionalities to 3D printed materials are envisioned as hollow glass sphere containing light weight composites or flame-retardant composites.

Concluding Remarks and Prospects

Functional and smart 3D (and 4D) printing of composites has attracted considerable attention and interest of the research community in a broad range of scientific and technological sectors. Combining the versatility of the different 3D printing technologies with the possibilities that composites offer in terms of functionality, open new paths for developments and research in this field.

Despite there are many works dealing with the different functionalities that can be induced in printed objects by tuning the composites, there are also many challenges (such as the porosity originated when working with composites that reduces the performance of the printed parts, or the increased difficulty for printing highly loaded composites, among others) that need to be overcome. Addressing the challenges associated with the development of functional and smart 3D and 4D printed composites will allow for obtaining high value products in high-tech sector such as electronics, robotics, aerospace, aeronautics, automotive, energy, and biomedicine.

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Halochromic Composite Materials

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Introduction

Certain chromotropic substances also known as smart materials detect physical or chemical conditions of an environmental influence such as change of temperature (thermochromism), penetration of water (hydrochromism), light irradiation of a specific wavelength (photochromism), pressure (piezochromism), polarity of a solvent (solvatochromism), application of an electric field (electrochromism), acid or basic character of a substance (halochromism) and others (Fukuda, 2007). The commonly used term -chromism refers to a color change, which is characterized by an irreversible (remains in the new state after reaction) or a reversible (returns to its nearly original state after reaction) color changing process (Bamfield and Hutchings, 2018). Chemical compounds which undergo an irreversible reaction process can store the influence in its color state. Halochromic substances have the functionality of pH indicators (acid/base) to determine pH changes in combination with a color shift (Peters and Freeman, 1995), which can be used to follow the course of a chemical reaction or to characterize the state of a chemical system. A change in color is caused by a different protonation state of the compound –different charge states at different pH values (Schwartz, 2002).

Conventionally, the color value of a pH indicator (in the form of a paper strip covered with a pH sensitive solution) is compared with a color reference (color scale) in order to determine the pH value of a substance with a known pH value. This color changing process can be detected with an optical reader using an image recognition algorithm or using a simple color comparison method such as a lookup table to compare it with a reference or database to get an indication of the degree of an influence. Halochromic substances in combination with other materials can extend the conventional spectrum of applications of the latter. In this way, harmful factors can be detected on a surface in the form of an intelligent coating that can initiate a surface healing process on the affected parts. Halochromic materials can be used as printable sensors to detect water penetration or in composite packaging to verify that products such as milk or meat are no longer suitable for human consumption. Halochromic substances can thus be used in combination with other materials to expand the range of functionalities of composite materials and to foster new applications. Several applications have already been developed at a technological stage, and others are currently under development. In this article, the characteristics, functionality and applications of halochromic materials are overviewed.

Chemical Reactions Involved in Halochromism

Acids and bases can be found in everyday life and in nature. Some examples are acid rain, formic acid as a defensive substance of ants, mineral acids such as sulfuric and nitric acids, in gastric juice for protein digestion, acidic foods such as salads, fruits such as oranges, kiwis or preservatives. They can also be found in alkaline soap solutions in the form of detergents or saponins in chestnuts, which serve as detergent alternatives. Halochromism refers to a color change in response to a change in the pH value of compounds or dyes that have the functionality of acid-base (pH) indicators (Fukuda, 2007). With pH-indicators the progress of a chemical reaction can be traced, the state of a chemical system can be characterized or identified, and it is used to measure the concentration of hydrogen ions or hydronium ions in a solution (Masterton *et al.*, 2012). Various indicators show a change between two or more colors – they show their colors depending on the pH value in acidic, neutral or alkaline solutions or materials. Acidic solutions have a pH value < 7 , basic solutions are in the range > 7 . Neutral solutions have a pH value of 7. Acid-base indicators themselves are low acids or bases, which can form anions or cations. Color changes are based on deprotonation of a color acid or protonation of a color base (halochromism). The color change is due to the structural changes of the compounds caused by the proton exchange, which lead to a color change of the substance (Bamfield, 2001). A color change is caused by different protonation states. In the acidic range, they are more strongly protonated than in the alkaline range (Carey and Sundberg, 2007). Depending on the number of transferred protons, one or more positive charges are added to the target molecule (protonated). As a result, the colorfulness can be attributed to the different charge states at different pH values since compounds change their color when accepting or releasing protons (Campbell and Farrell, 2007). When a hydroxy group of a phenol (Phenols are compounds of a hydroxyl group ($-OH$) which are bound to an aromatic hydrocarbon group) is deprotonated, the resulting free electron pairs of the phenolate group participate more strongly in resonance (resonance structures) (Resonance describes that binding conditions cannot be represented by a single structural formula) with the result that the absorption maximum shifts due to the negative surplus of charge from the invisible (UV) towards the visible part of the spectrum (VIS) (Nassau, 2001).

The more delocalized the electrons are, the easier they can absorb the energy of the light (Scotter, 2015). Due to the halochromic effect, some dyes can be used as acid-base indicators, e.g., phenolphthalein, methyl red, methyl orange, and bromothymol blue dyes. Some chemical compounds are invisible (colorless) and only visible at a certain pH value (such as crystal violet lactone). Phenolphthalein is also colorless (Fig. 1) in lightly acidic or neutral environments, whereas it shows a purple color in an alkaline environment (Nassau, 2001). In a weakly alkaline environment ($pH > 7$) a phenolic hydroxyl group of phenolphthalein releases a proton, resulting in an anion (Anions are formed from atoms or molecules by electron absorption or release of hydrogen ions H^+ (protons)).

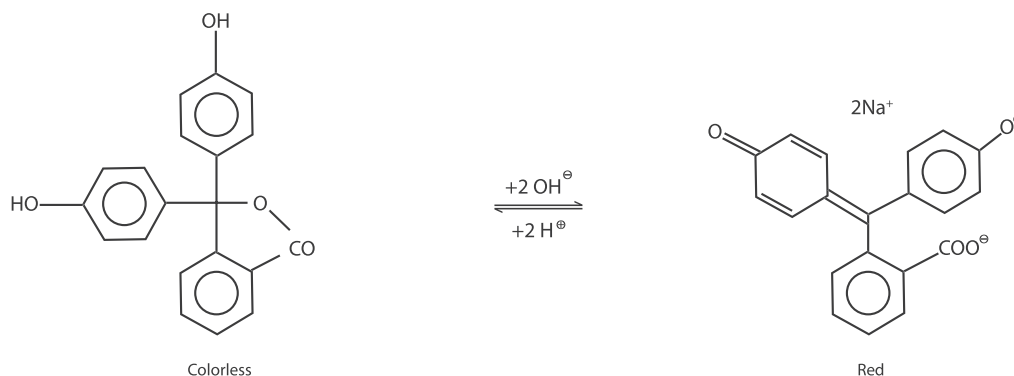


Fig. 1 Halochromic forms of phenolphthalein.

Cyanidin is a natural organic compound and dyestuff and is suitable as an indicator (Blank, 1947). It belongs to the group of anthocyanins; pelargonidin ($C_{15}H_{11}O_5^+$), cyanidin ($C_{15}H_{11}O_6^+$), delphinidin ($C_{15}H_{11}O_7$), malvidin ($C_{17}H_{15}ClO_7$) belong to this group (Fig. 2). Anthocyanidins undergo a pH-related reaction, each structure showing a different color. With an increasing number of hydroxyl groups (dotted) the color changes from red to blue. Full removal of the hydroxyl group causes a yellow color shift (Onslow, 2014).

The color of cyanidin (Fig. 3) ranges from reddish-purple ($pH < 3$; the cyanidine molecule binds a proton thus yielding a cyanidine cation) to purple ($pH 6-7$) to blue ($pH 7-8$; the cyanidine molecule releases a proton; deprotonation), and from green ($pH 9-11$; the release of a second proton even results in a dianion) to yellow ($pH > 12$). Yellow is a color that indicates the irreversible destruction of cyanidin - the molecule is irreversibly converted to a yellow chalcone anion. The color change of the red cyanidin is thus based on two $-OH$ groups that release protons. Cyanidin can be found in many different plants in a glycoside form (as anthocyanin) such as red cabbage, cherries, red roses, blueberries, raspberries and blackberries (Bechtold and Mussak, 2009). In cornflowers, the anthocyanidin dye is chemically bonded to other ions such as Fe^{3+} or Al^{3+} . Hydrangeas possess a flower color that depends on the pH value of the soil.

Application of Halochromic Materials

The processability of halochromic materials such as pigments or dyes can be achieved by embedding these compounds in a carrier (matrix). In order to combine a composite material with an intelligent material, it is necessary to identify the processing steps required to realize a comprehensive linking system. This section deals with technical aspects of inkjet printing and the requirements for an inkjet ink formulation.

Furthermore, this section deals with the use of microencapsulation for the targeted use of halochromic materials. Technical limitations and limitations are highlighted.

Inkjet Printing

Inkjet printing is used in several industrial sectors. Traditional printed products are often two-dimensional paper products, whereby the printing technology advances in the field of three-dimensional object printing. The inkjet printing process is used in several industrial sectors such as the automotive industry for automotive coatings, dashboards, speedometers, and the electrical industry for printable circuits, electronic sensors, antennas, and many more. Inkjet printing belongs to the category of Non Impact Printing (NIP). Printing processes (Fig. 4) frequently used in industrial inkjet printing are continuous inkjet (CIJ) and drop-on-demand (DOD). Drop-on-demand (DOD) is subdivided into thermal DOD and piezoelectric DOD. The continuous inkjet process is an inkjet printing process in which a continuous ink jet is generated to produce a fitted outlet pressure. This process takes place inside the print head where a piezoelectric actuator controls the printing process, and modulates the inkjet until a continuous jet of microfine ink droplets exits the print nozzle and is jetted at a high pressure and a correspondingly calculated speed into the direction of the substrate. A relevant factor here is the electrical conductivity of the ink since flowability must be ensured. This is also important for subsequent electrical charging and deflection of individual ink droplets. In order to control the ink droplets, they pass through a charged electrode with an electric field located directly behind the outlet nozzle where the droplets are electrically charged. The ink stream passes through the deflection plates, where the charged ink droplets are electrostatically deflected. During this process, the excess and unused droplets are deflected into a reservoir, from which they reintegrate into the ink cycle by passing a filter unit and a pump.

In the drop-on-demand process, an ink drop is ejected according to the requirements by the creation of a pressure pulse. A water-based or solvent-based inkjet ink is protected against leakage by means of negative pressure. A piezoelectric effect, a voltage-dependent piezo actuator that can deform under electrical voltage, presses the ink through the nozzle. Another possibility is the bubble process (bubble jet), which uses a resistance heating element to temper the ink to a temperature range of 300–400°C for

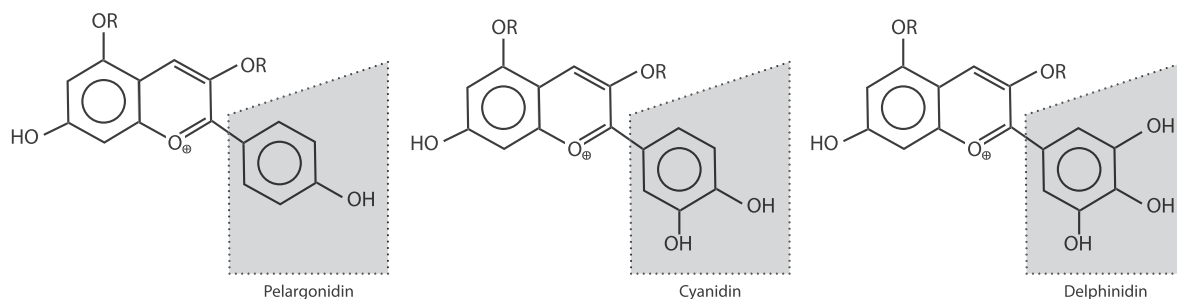


Fig. 2 Group of anthocyanins with typical structure variations.

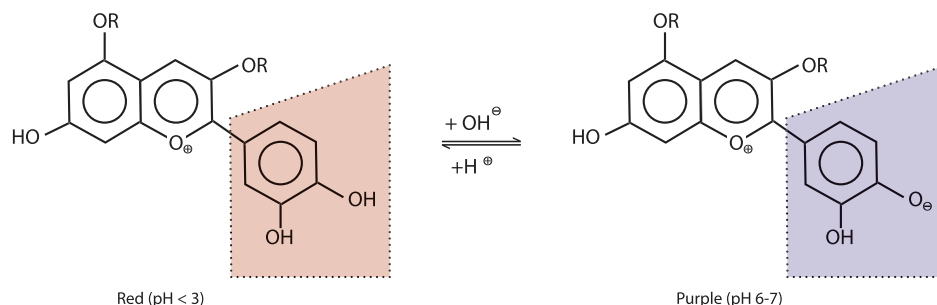


Fig. 3 Halochromic forms of cyanidin/R = glycoside.

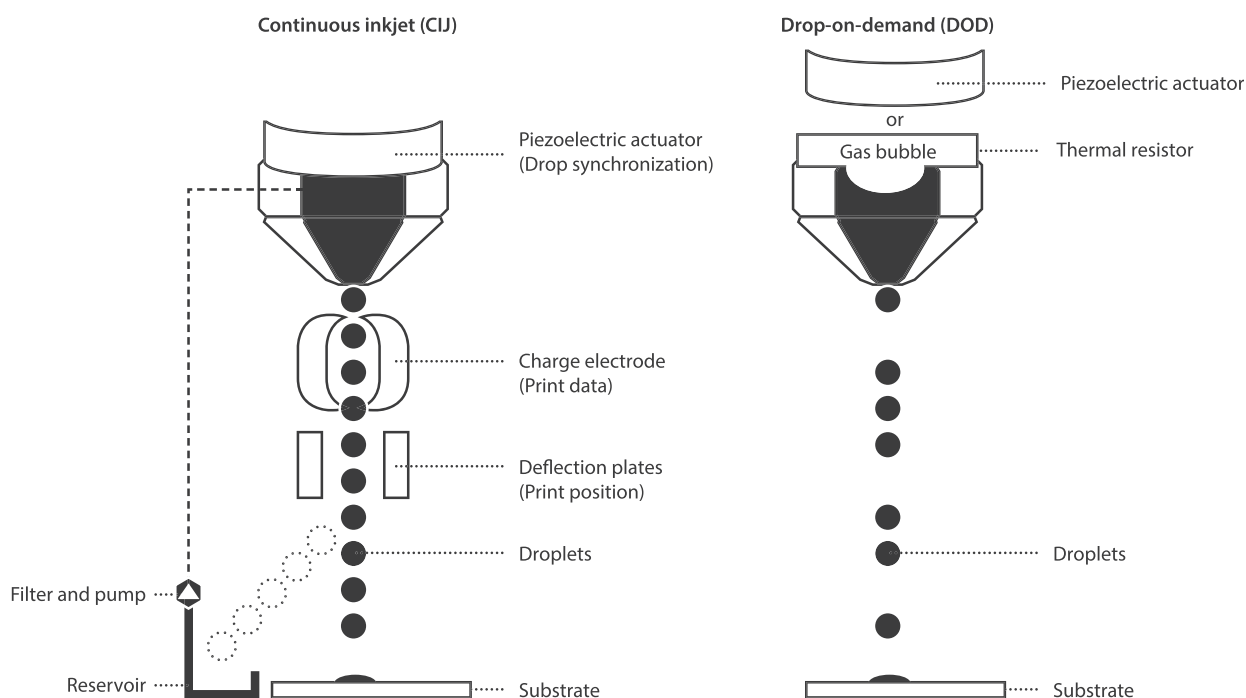


Fig. 4 Industrial inkjet printing.

few microseconds during printing (Cui *et al.*, 2012), causing a thin film of ink to vaporize over the heater and push out a droplet of ink from the nozzle. Halochromic inks should be protected against high temperature, otherwise they get impaired or damaged. For example, anthocyanins suffer from very high thermal sensitivity. The decay rate of anthocyanins increases with increasing temperature (Giust and Sigurdson, 2019). Many factors have to be considered in order to develop a permanently stable ink for inkjet printing. Disturbing time-related changes such as particle deposition, agglomeration, phase separation and other issues must be prevented. When developing inkjet inks, factors to be considered are viscosity, surface tension, pH value, dielectric properties (conductivity), dye/pigment concentration, foam formation (defoamer) and others, which are not discussed in detail here.

Microencapsulation

Nature is a role model for many high-tech innovations, including composites such as wood, based on long cellulose fibers, which are bonded together by a group of phenolic macromolecules of lignin (Calvo-Flores *et al.*, 2015). In comparison, cotton, which does not contain lignin, is mechanically weaker. Different means of encapsulation such as the shells of nuts, fruits or eggs of animals such as snakes, birds or the spawn of frogs or fish can be found in nature, aimed at protecting the inner material against the surrounding environment.

Microcapsules consist of a core (Fig. 5), in which micron-sized ($> 1 \mu\text{m}$) droplets, particles or gases are enclosed in a protective, spherical or non-uniformly shaped shell. They have a wide range of functions and applications in the field of cosmetics, detergents, agriculture, food, coating industry and more. Depending on the application, the inner core contains pigments, dyes, indicators, catalysts, hardeners, flame-retardants, aromas, etc., whereas the shell often has a protective functionality. Depending on the selected material, the shell can be made permeable, semi-permeable or impermeable to the external environmental conditions (Ghosh, 2006). The shape of a microcapsule often depends on the form of the core, where the size of a microcapsule is an important factor for processability and industrial applications. Microencapsulation differs in three typical variants. The mononuclear type is based on an encapsulated core. Another type of encapsulated form is Polynuclear encapsulations. Finally, in matrix encapsulation, the core material is homogeneously dispersed into the shell material. Other mononuclear forms with poly shells and other forms are also possible (Giamberini *et al.*, 2015).

Technological applications are the controlled or sustained release of the core material under predefined conditions and use of composites made of two different types of materials to create different functionalities. One popular microencapsulation product is carbonless copy paper. Fig. 6 shows that colorless leuco dye called crystal violet lactone layer encapsulated at the underside of the top sheet gets destroyed under pressure and, as a result, it is transferred to the copy. The crystal violet lactone reacts then with the top of the lower sheet, coated with an acidic compound, by initiating the opening of its lactone ring and yielding a blue-violet triphenylmethane color (Ferrara and Bengisu, 2014).

Methods and Processes

In the following, the procedure for color detection is demonstrated in an experimental setting using halochromic materials (Table 1) as example. In this way, important requirements for accurate detection of colors, the respective characteristics, and color change phenomena are briefly outlined.

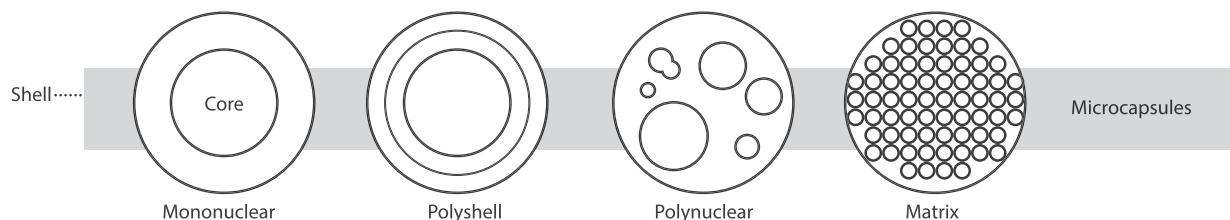


Fig. 5 Types of microcapsules.

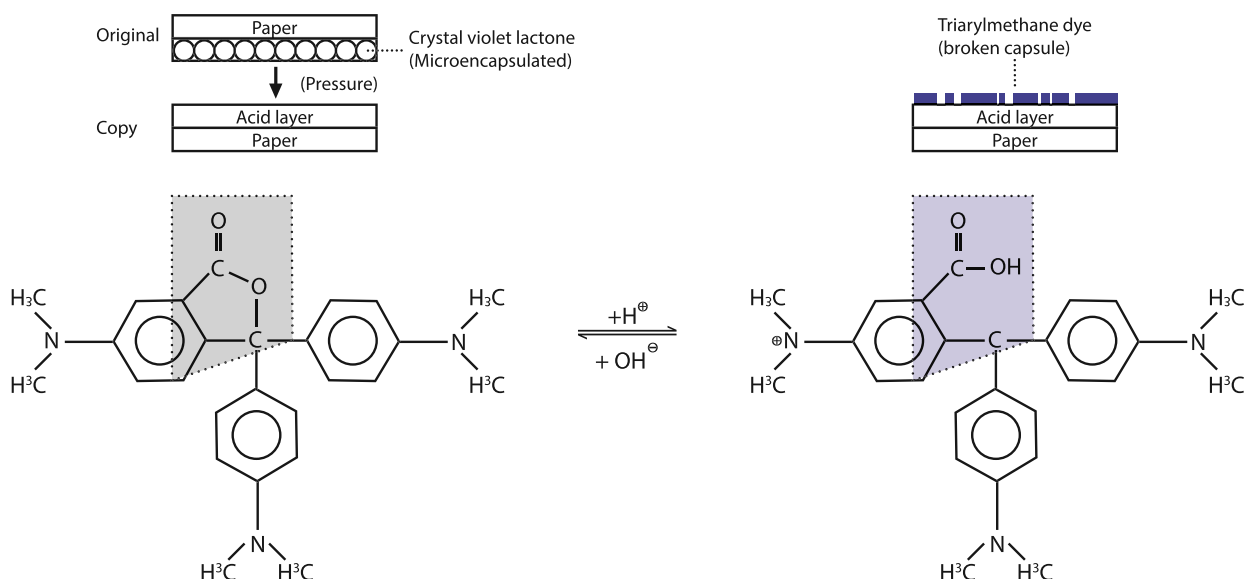


Fig. 6 Microencapsulation of crystal violet lactone.

Table 1 Materials for the experimental setting

Substrate	Print paper A (inapa tecno oxygen pure) Format: DINA 4, Weight (ISO 536): 80 ± 3.0 g/m ² , CIE whiteness (ISO 11475): 150 ± 3.0 , Brightness (ISO 2470): $104\% \pm 3.0\%$, Opacity (ISO 2471): 92.0%, Thickness (ISO 534): $106 \text{ mm}/1000 \pm 3.0$, Stiffness longitudinal/transverse (ISO 2493): 80/45 mN, Roughness (Bendtsen, ISO 8791–2): 220 ± 50 mL/min Print paper B (BalancePure) Format: DINA 4, Weight (ISO 536): 80 ± 3.0 g/m ² , CIE whiteness (ISO 11475): 148 ± 3.0 , Brightness (ISO 2470): $100\% \pm 3.0\%$, Opacity (ISO 2471): 92.0%, Thickness (ISO 534): $100 \text{ mm}/1000 \pm 3.0$, Roughness (Bendtsen, ISO 8791–2): 150 ± 50 mL/min, Specific volume (ISO 534): $1.25 \text{ cm}^3/\text{g}$ Chromo-duplex-carton (Multicolor Mirabell™ -MCM/GD2) Format: DINA 4, Weight (ISO 536): 250 ± 3.0 g/m ² , Thickness (EN 20534): $340 \text{ mm}/1000 \pm 3$, Stiffness longitudinal/transverse (DIN 53121): 15.4/15.4 mNm – 15%, Specific volume (EN 20534): $1.36 \text{ cm}^3/\text{g} \pm 5\%$
Dyes	Anthocyanin (grape skin extract, food dye, E163) Litmus (CAS: 1393-92-6) Indicator solution Unisol (113)
Solvents	Ethanol (C ₂ H ₆ O, CAS: 64-17-5)
Additives of the ink	Humectants: Glycerin (C ₃ H ₈ O ₃), Urea (CH ₄ N ₂ O) Surface tension regulator: Alkyl sulfonate, Alkyl polyglycoside Antifoaming agent: Polydimethylsiloxane (C ₂ H ₆ O ₂ Si)
Filtration equipment	Millex-SV (SLSV025LS): Pore size: 5.0 μm Maximum inlet pressure: 5.2 bar (75 psi) Hold-up volume: <0.1 mL Filtration area: 3.9 cm ² Material: Hydrophilic Polyvinylidene Fluoride (PVDF)
Instruments	Piezoelectric inkjet printer (Epson WorkForce WF-3620) Print head: PrecisionCore Thin Film Piezo element: 1/1000 mm Droplet Size: 2.8 pl (range of 1.5–32.5 picoliters) Nozzle Configuration: 800 Nozzles Black (K), 256 Nozzles per Color (CMY) Printing Resolution: 4800 × 2400 DPI Spectral-densitometer (TECHKON SpectroDens) Polarizing filter: off Type of light: D50, 2° standard observer Diameter of measuring orifice: 3 mm

Conditions and Criteria for Color Recognition

The ability of the untrained human eye to perceive color can be error-prone and subjective, so electrochemical or optical measurements are better suited to obtain reliable data. The ISO 3668:2009 standard specifies how colored materials are to be evaluated in the manufacturing industry (textile industry, automotive industry, etc.). The graphics industry, on the other hand, is described in ISO 3664:2009, where the focus is on visual color management. Standardized Illuminant D50 with 5000K (Illuminance >2000 lux $\pm$ 250 lux, to visualize minor color differences at a wavelength range between 300 and 780 nm at a distance of 5 nm) is used for the entire manufacturing process from prepress to press. Two-dimensional samples are sampled under an illumination of 0° and a viewing angle of 45° (measuring geometry 0°/45° or 45°/0°). Different brightness leads to a different color impression whereby reflections and shine effects lead to misinterpretations. Color differences are indicated according to the ISO rating scale by hue, chromaticity (saturation) and brightness.

Materials and Instruments

Color Changing Behavior

In the following, the functionality of halochromic materials is demonstrated using selected organic substances, namely anthocyanins, litmus and a universal indicator (Unisol). These substances (Table 1) are embedded in ethanol –excluding Unisol, which is in liquid state– in the form of a prototype ink for inkjet printing. Additionally, additives are used (described in “Materials for the experimental setting”, Table 1) to adjust the properties of the ink for inkjet printing. Particles >5.0 μm are filtered through a filter unit before filling the ink cartridge into the piezoelectric inkjet printer. The following acids and bases are used for the activation process: Base: Na₂CO₃ (disodium carbonate, soda) 1.0 g in 20 mL H₂O, pH = 11; Acid: Citric acid (2-Hydroxypropane-1,2,3-tricarboxylic acid) 3.0 g in 20 mL H₂O, pH = 3.

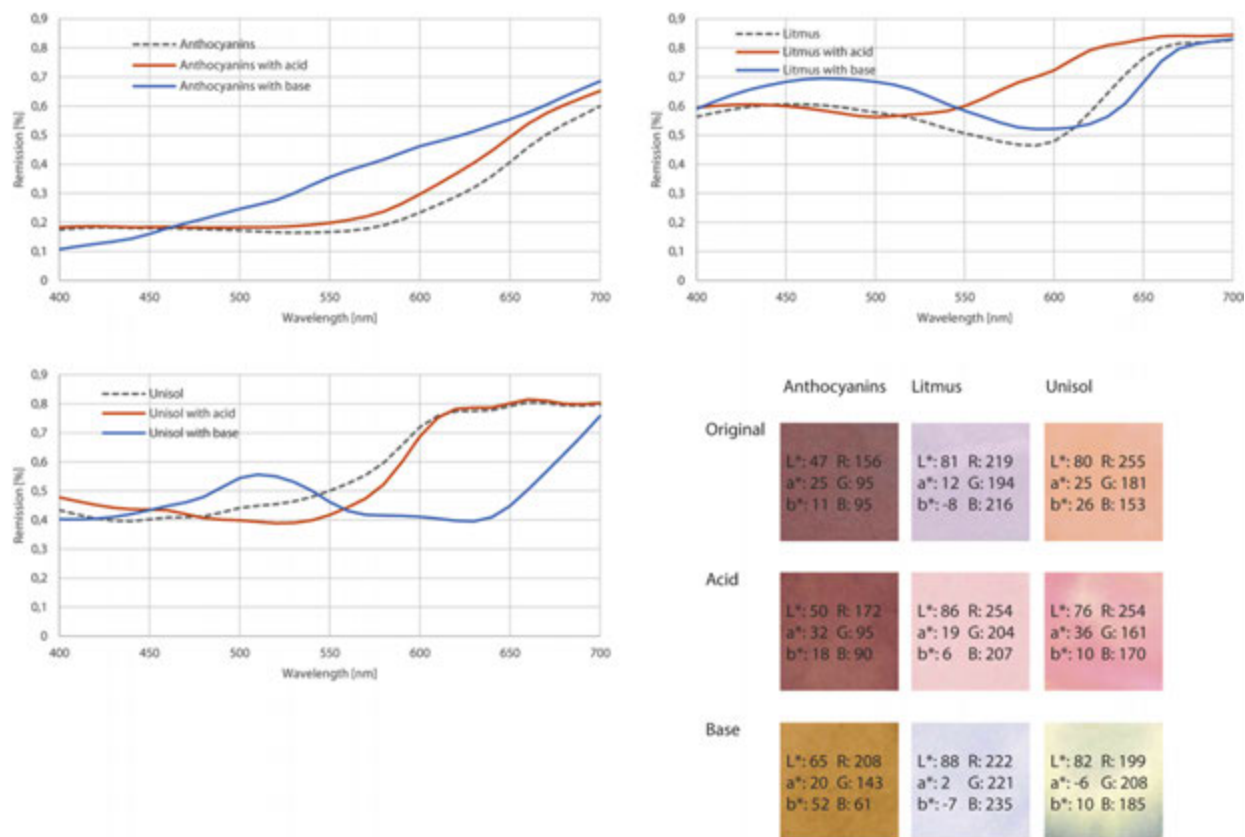


Fig. 7 Remission, L^*a^*b and RGB values of inkjet printed halochromic surfaces.

Light is a radiation, which consists of electromagnetic oscillations that spread out in waves. The distance between these oscillations is described as wavelength. The spectrum of visible light (VIS) ranges from about 380 to 720 nm. Within this VIS range, the wavelength determines the color appearance. Thus, red is located at around 650 nm, green at around 550 nm and blue at around 450 nm. The graph shown in the figure (Fig. 7) is the remission curve, which describes at which wavelengths (λ) remission (β) is present. The remission curve is characteristic for each color. The spectral remission curve $\beta(\lambda)$ is used to describe surface colors. The color of an object, as well as of surfaces, depends on how much of the incoming light of the different wavelengths is absorbed, transmitted or reflected. The reflectance curve describes the reflected amount of incoming radiation, which can be plotted in a coordinate system depending on the wavelength. The spectrophotometer used in this experiment (Table 1) measures the surface color by illuminating the surface with a defined light source. The entire spectrum of visible light is separated into a number of small bands (nm) called reflectance values, from which a reflectance curve is plotted. This allows defining the exact color location within the color space and calculating color deviations between two measuring points. This physical principle is used as a basis for color reproduction in the printing sector. In this way, the remission curves (Fig. 7) before and after a chemical reaction can be measured using a spectral densitometer. The remission curves of the three halochromic materials, namely anthocyanin, litmus and Unisol are measured in the original, acidic and basic ranges. Anthocyanin shows, under acidic conditions, an increase of its remission at about 520 to 700 nm, and thus the imprinted color becomes brighter in the red range. Note that when the three color channels (red, green, blue) are specified as 0.0.0, we have black color, and the opposite is the case for 255.255.255, which gives white color. This means the higher the value, the brighter the color channel is. This is also visible in the RGB values, where the original shows a red (R) value of 156 and the acid reaction a red value of 172. After a basic reaction, the wavelengths decrease from 400 to 460 nm and increase from 460 to 700 nm. This results in a wavelength shift and a change in color from blue (B) to yellow.

There are two important effects to pay attention to: Bathochromic and Hypsochromic effects. The former describes a redshift of the absorption spectrum into the longer wavelength, i.e., lower energy range of the electromagnetic spectrum. The latter describes the blue shift of the absorption spectrum into the shorter wavelengths, i.e., the energy-rich region of the electromagnetic spectrum.

Litmus changes its wavelength after acidic conditions, from 520 to 680 nm with an increase of its intensity in remission – with a color change to salmon-pink (254.204.207). After being subject to basic conditions, its remission increases from 400 to 550 nm and decreases from 550 to 660 nm with a color change to light purple (222.221.235). Finally, Unisol, changes its wavelength from 400 to 470 with an increase in remission, and from 470 to 610 with a decrease in its remission under acidic conditions – it changes

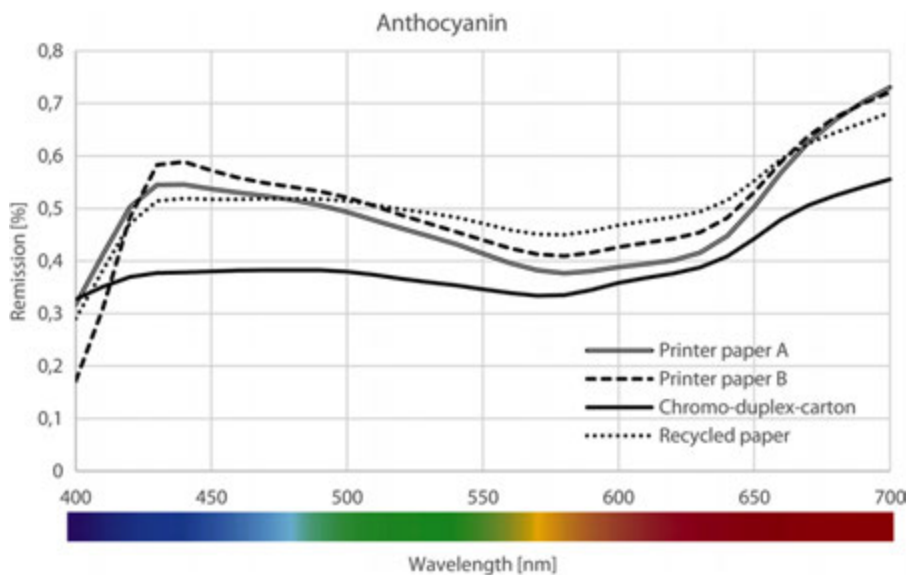


Fig. 8 Types of papers and their influence on the pH indicator.

from orange (255.181.153) to red (254.161.170). After being subject to basic conditions, it changes its wavelength with an increase in remission from 440 to 540 nm and a decrease from 540 to 700 nm with a color change to yellow-green (199.208.185).

Based on the color values in $L^*a^*b^*$ or RGB, it is possible to detect the color changes by an optical reader and compare them with a pH scale. The respective color deviation can be displayed and analyzed as ΔE in the CIE $L^*a^*b^*$ color space. In the case of non-neutral substrates, the pH fields vary in their color. It is therefore necessary to calibrate them to a large number of pH values (entire scale). Thus, different materials from the acid to the basic ranges can be used for calibration.

In **Fig. 8**, anthocyanin with a uniform concentration is used to demonstrate the influence through the paper pH on the indicator dye. The paper itself is acid-sensitive, because the acid contained in the paper splits cellulose into small molecule units over time, causing the paper to loss flexibility and tear resistance.

Papers have different pH values. This is often due to the pigments and the fillers of the paper. Coating suspension usually consists of white pigments and binders. Pigments of kaolin and calcium carbonate endow the paper with an absolutely closed and uniform surface. Calcium carbonate has a pH value of 7–9 and kaolin has a pH value of 4–9 (saturated solution at 20°C). Precipitated calcium carbonate is used as filler in the paper pulp:

- (1) $\text{Ca}(\text{OH})_2 + \text{CO}_2 - \text{H}_2\text{O} = \text{CaCO}_3$
- (2) Calcium hydroxide + carbon dioxide – water = precipitated calcium carbonate (PCC)

Calcium carbonate gives the paper maximum whiteness and density, increases the volume and improves printability and light fastness. Casein or starch is usually used as a binding agent for the adhesion of the pigments and to increase water resistance of the coating. Pigmentation means a mineral surface application on the uncoated paper of up to 5 g/m² (DIN 6730). In order to control the pH of papers used as indicators, which should be near zero-point (Siebel *et al.*, 1953), acidity determinations must be carried out. Acid-free papers have a pH value close to seven and can be produced from any cellulose fiber as long as the active acid pulp is removed during processing.

Applications

Chromotropic substances such as halochromic materials can be used for smart sensors that autonomously measure real time data from their local environment over an extended period. An optical scanning process can measure color-changing processes (Bilgin and Backhaus, 2019) of the halochromic materials and other smart materials using the camera integrated into a smart device (e.g., smartphone). Smart devices can connect over TCP-IP to an autonomous network (Internet of Things), where the measured data can be transferred to a server, which evaluates them and tracks the history of the sensors (Bilgin and Backhaus, 2017). Halochromic materials can be embedded into an inkjet ink matrix in order to be printed by an inkjet printing process. An essential advantage is that the printable (chemical-physical) sensors are independent of electronic components, which means that they are suitable for long-term measurements, without circuits or energy sources (Bilgin and Backhaus, 2018).

As in **Fig. 6**, halochromic materials can also be used as pressure-sensitive sensors that break from a predefined pressure load to mark the substrate or synthetics in color. Halochromic materials such as bromothymol blue (triphenylmethane dye) can behave like a thermochromic material when embedded in a responsive polymer matrix (Seeboth *et al.*, 2010). Therefore, it is possible that the triphenylmethane dye becomes sensitive to temperature changes in combination with the pH change of the polymer matrix.

This causes the color of the pH indicator to change through the surrounding medium. This is because pH-reactive polymers can cause a pH change via protonation or deprotonation of the functional groups of the polymer chains (Kocak *et al.*, 2017). These thermochromic polymer materials represent a paradigm in the field of non-toxic thermochromism because they can be sustainable and environmentally friendly smart materials. For example, the thermochromic material presented in the work of Seeboth *et al.* (2013) is based on a biopolymer of polylactic acid (PLA), a natural dye from the halochromic group of anthocyanidins (E163), a dodecyl gallate (E312) derivative and a fatty acid (E570). The thermochromic effect is caused by a conformational change –a change of the three-dimensional structure induced by a change in pH– of the polymer structure, which reversibly initiates the formation of a polymer dye complex (*ibid.*). A wide range of smart materials are environmentally harmful or hazardous, therefore it is essential to use materials that are environmentally friendly.

A further example of an application can be found in the case of offshore wind turbines, which are exposed to extreme weather conditions such as snow, rain, heat and UV radiation. Raindrops, for example, attack the rotor blades and erode the surface. Welding seams at the basement of offshore wind turbines have large weak points at which cracks can occur and algae and mussels can adhere (Koch and Schwarz, 2016). Several functional coatings with antifouling and antibacterial functionalities based on pH reactive coatings can be used to reduce harmful environmental effects.

pH-reactive properties to control antifouling and antimicrobial properties in marine environments have already been investigated on the basis of three different types of multilayer films (polyethylene, polyvinyl alcohol and alginate) containing capsaicin. The three types of films can control capsaicin release at low levels in alkaline solutions and cause rapid release in acidic solutions (Hao *et al.*, 2020). pH-reactive nanocapsules were produced from capsaicin and chitosan, which showed a controlled release of capsaicin in alkaline solutions. In the transition between protonation and deprotonation of pH-sensitive functional $-NH_2$ groups in chitosan, capsaicin can be triggered to self-release, if the pH-value changes due to bacterial propagation. Depending on the pH value of the surroundings, which can be acidic or alkaline, the nanocapsules may expand or contract because of the protonation or deprotonation of chitosan and release capsaicin (Wang *et al.*, 2018). Another useful application of halochromic materials are smart corrosion inhibitors in the form of a corrosion protection coating. In addition to corrosion retardation and corrosion protection, corrosion detection by means of a visual representation is also an important aspect of autonomous early corrosion detection, in which hidden corrosion is indicated. Additionally, pH indicators such as phenolphthalein or bromothymol blue could be added to an acrylic-based coating to alert from corrosion. With the increase in pH, a change in color was observed by Zhang and Frankel, which was caused by a cathodic reaction, enabling the identification of a corrosion process (Zhang and Frankel, 1999). Another application of phenolphthalein in the form of a coating can be found in Maia *et al.* (2013). The coating was able to detect active corrosion processes on different metallic materials. Corrosion detection based on a color change in active cathodic zones results from the interaction of hydroxide ions with phenolphthalein. In the work from Maia *et al.*, materials were encapsulated in mesoporous silica nanocontainers, which are semipermeable to water molecules and ions.

Conclusions

Many chromotropic materials, such as halochromic materials, are capable to detect external environmental influences. In composite materials, halochromic substances can detect harmful factors on a surface in the form of an intelligent coating. This makes it possible to initiate a surface healing process to repair the affected parts. Halochromic materials can be used as printable sensors and other applications as briefly overviewed here. Chemical processes behind acid-based color change were presented and dyes, which are already particularly amenable for this application, were outlined within this article. Processing of halochromic materials and requirements for their optimal use were shown. In particular, inkjet printing and microencapsulation were shown. A practical example was also presented to illustrate the behavior of halochromic materials. Several substances were printed by inkjet printing and their color change was examined and evaluated. A method of analysis based on RGB or $L^*a^*b^*$ color space (optical readout) was presented. Not only halochromic dyes can be used in plastics as an indicator, but also their pH value can regulate or adjust the properties of the plastic themselves. Thus, halochromic substances and composites can be used for a myriad of purposes and applications.

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Smart Protection of Carbon-Reinforced Composite Materials and CFRP-Metal Joints

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Introduction

Due to the high demand for weight optimized structures to meet the low emission goals of the transport sector (principally the aeronautical and automobile industries), carbon fiber reinforced polymers (CFRPs) are increasingly employed in multi-material assemblies comprised of CFRPs and a variety of high-performance alloys. When used alone under certain service conditions CFRPs can be prone to degradation; a phenomenon that is aggravated on galvanic coupling to metallic alloys in the presence of moisture, as in CFRP-metal joints. To mitigate against such degradative tendencies there is need to understand the possible operative degradative mechanism(s) in each constituent of such multi-material assemblies, in order to sense/detect, monitor and predict degradation in multi-material assemblies, and hence develop smart strategies for their protection from degradation.

Fiber reinforced polymer composites are employed in a variety of applications in which damage can manifest as degradation and failure of the matrix phase, the reinforcing fibers, the interface, and/or the entire composite structure. Irrespective of the genesis or presentation of degradation in composite structures there is a need to sense, monitor, and predict material degradation and failure in fiber reinforced polymer composites and multi-material assemblies, in line with the practice with structures composed of metals and alloys. Potential methods for sensing and monitoring fiber reinforced polymer composite degradation are dependent on a variety of factors such as the composition of the constituent phases of the composite(s) with respect to differences in such physical properties as electrical conductivity, moisture uptake, gas permeability, and mechanical properties under anticipated service conditions (lowered or elevated temperatures, presence or absence of moisture, and stresses), and possible coupling with metals as in CFRP-Metal joints. This work reviews literature on detection and sensing of material degradation in fiber reinforced polymer composites and classifies reported methods with respect to electrical properties of composite constituents (conductive matrix + non-conducting fiber, non-conductive matrix + non-conductive fiber, and conductive matrix + conductive fiber), mechanical properties, and service conditions, highlights the challenges inherent in sensing material degradation in composite structures, and give perspectives on plausible approaches to sensing, monitoring and smart protection of material degradation in fiber reinforced composite systems and multi-material assemblies.

Methods of Joining Composites to Each Other and to Metals and Implications for Degradative Processes

Three techniques; adhesive bonding, mechanical fastening, and a combination of bonding and fastening are reported to be popular for joining of composite materials to each other and to other materials like metals (Smith, 2005). Besides these, other methods used to join metals to polymer composites include; friction spot joining (Esteves *et al.*, 2015, 2012; Amancio-Filho *et al.*, 2011), ultrasonic welding (Balle *et al.*, 2009), laser welding (Tan *et al.*, 2015; Xianghu *et al.*, 2013; Katayama and Kawahito, 2008), and clinching (Lee *et al.*, 2014). For more information on the wider variety of methods for joining composites to metals these references (Amancio-Filho and Dos Santos, 2009; Kellar and Worrall, 2016; Costa *et al.*, 2012; Pramanik *et al.*, 2017) are recommended.

Recent developments in composite and adhesive constitutions by addition of conductive nano-fillers (Ofoegbu *et al.*, 2019a; Haq *et al.*, 2019; Haq, 2019) in the so called “active adhesive technology” (Haq *et al.*, 2019; Haq, 2019) though yielding some important advantages like possibility of local heating and repair, and health monitoring can make carbon fiber reinforced polymer composites more susceptible to galvanic corrosion on coupling with metals due to the conductive nano-species added to the adhesive employed in joining composite parts to each other and to metals. Though incorporation of conductive nano-species into polymer composites above the percolation threshold markedly improves the electrical conductivity (Lonjon *et al.*, 2012), the thermal conductivity is not much enhanced (Shenogina *et al.*, 2005). Hence the addition of conductive nano-species whilst enhancing the possibility of galvanic corrosion might not enhance dissipation of heat that could arise from joining operations.

Sources of Damage to Carbon-Reinforced Composite Materials and CFRP-Metal Joints

Damage to carbon-reinforced composite materials and CFRP-metal joints can be due to defects introduced during its manufacture or to its interaction with degradative factors under its service conditions. In this work the focus is on damage encountered under service conditions. For information on defects introduced into these class of materials during its manufacture these references (Potter, 2009; Fischer *et al.*, 2015; Hassan *et al.*, 2017; Liu *et al.*, 2019; Boisse *et al.*, 2016; Ares *et al.*, 2018; Stamopoulos and Di Ilio, 2019) are recommended. It is important to emphasize that the mechanism of damage is dependent on the service conditions, and distinct from the presentation of damage. However, damage due to different mechanisms can share some similarities in their respective presentations.

Carbon-fiber reinforced composites and CFRP-metal joints can suffer damage under service conditions due to impact, static overload, fatigue, hygrothermal effects, creep, galvanic corrosion, and thermal effects such as overheating and/or lightning strike (Ofoegbu *et al.*, 2019a; Mahato *et al.*, 2014; Kumar *et al.*, 2002) or combinations of these. Damage to CFRPs due to these factors manifest principally as cracks (matrix damage), delaminations, fiber buckling/pull-out or fracture, interfacial failure in the matrix-fiber interface, moisture uptake/ingress, matrix erosion, dis-bonding and adhesive creep in adhesive bonded parts. Having identified the principal sources and manifestations of damage in carbon fiber reinforced composites and CFRP-metal joints, their consequent respective implications on the physical, mechanical and electrical properties of composites are reviewed with a focus on the impact of these changes on smart damage detection and protection in terms of the respective damage mechanisms, and then in terms of the presentation of the damage(s).

Impact Damage

Impact damage to CFRPs are due to its interaction/exposure under service conditions to impact loads (short duration forces) in which energy is transmitted into composite structures during a short time interval. Such pulsed transmission of energy can cause significant damage to composite structures and composite-metal joints. Impact damage can present as disbonding (Ali *et al.*, 2017), local substructure damage (Kim and Kedward, 2000), matrix cracking (Aymerich and Meili, 2000), and delamination (Kim and Kedward, 2000), Fig. 1; all of which lead to some reduction in the mechanical properties of composite materials. The actual presentation or mode of failures due to impact damage in fiber reinforced polymers is markedly dependent on the energy absorbing capability of the composite which is in turn significantly influenced by the matrix properties (Cantwell and Morton, 1991). For example, major sources of impact loading of composite aeronautical structures under service conditions include bird strikes on aircrafts (Di Caprio *et al.*, 2019; Airolidi and Cacchione, 2006; Orlando *et al.*, 2018; Tang *et al.*, 2019), hail/ice impact (Kim and Kedward, 2000; Anghileri *et al.*, 2007) or tool drop during aircraft assembly. The energy dissipated on impact (which can cause damage when higher than the failure threshold energy (FTE)) is directly proportional to the mass of the impactor and to the square of the impactor velocity at impact. Since impact damage emanates from dynamic force(s) and much more dependent on the velocity of the impacting force, it can be used as a criterion for classifying impact events/damage into; quasi-static (≤ 1 m/s) (Ali *et al.*, 2017; Sutherland and Soares, 2012; Li *et al.*, 2017), low velocity (of speeds 1–10 m/s) with energies in the range of 50 J (Ali *et al.*, 2017; Davies and Olsson, 2004; Shivakumar *et al.*, 1985; Mahdi *et al.*, 2017; Farooq and Myler, 2015), intermediate velocity (≥ 10 –10 m/s) and with energies ≥ 50 J (Davies and Olsson, 2004), high velocity (≥ 300 –2500 m/s) with energy in the range of 10–20 kJ (Kim and Kedward, 2000; Davies and Olsson, 2004; Safri *et al.*, 2018; Liu *et al.*, 2020b), and hyper velocity ($\leq 30,000$ – $\geq 70,000$ m/s) (Davies and Olsson, 2004; Safri *et al.*, 2018; Razali *et al.*, 2014) impact events/damages. Unlike metallic materials, impact damage to composite damage can be often difficult to detect visually. Hence, impact damage to composite materials is monitored by non-destructive imaging (NDI) techniques like ultrasonic testing, optical thermography and sonic infrared thermography (SIR) (Gaudenzi *et al.*, 2014; Meola and Carlomagno, 2014; Maierhofer *et al.*, 2014), Visual Testing (VT), Ultrasonic Testing (UT), Radiographic Testing (RT), Electromagnetic Testing (ET), Acoustic Emission (AE), and Shearography Testing (Gholizadeh, 2016; Růžek *et al.*, 2006), Mechanical Impedance Analysis (MIA) (Capriotti *et al.*, 2000; Heida and Platenkamp, 2011), and electro-mechanical impedance (EMI) (Cherrier *et al.*, 2013; Opoka *et al.*, 2013; Perez *et al.*, 2014; Gresil *et al.*, 2012; Djemana and Hrairi, 2017; Tawie *et al.*, 2019).

Static Overload

Damage to CFRP and CFRP-metal joints due to static overload occur when a static (or quasi-static) load beyond its mechanical strength is applied. The presentation of damage/failure due to static overload is dependent on the nature of the load (tensile,

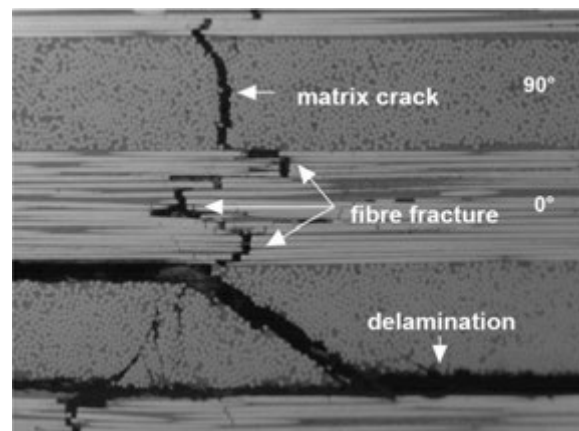


Fig. 1 Principal damage types in impacted fiber reinforced laminates. Reproduced with permission from Cambridge University Press from Davies, G.A.O., Olsson, R., 2004. Impact on composite structures. *The Aeronautical Journal* 108 (1089), 541–563. doi:10.1017/S0001924000000385.

compressive or flexural), fiber orientation with respect to applied load and matrix/adhesive properties. Generally, damage response of CFRPs due to static/quasi-static overload are similar to that observed for low velocity impact loading (Kumar *et al.*, 2017; Hiley, 1999; Korneeva *et al.*, 2017; Romhányi *et al.*, 2017). Damage due to static overload can present as fracture of the reinforcing fibers by fiber cleavage, buckling or shearing (depending on type of stress applied i.e. tensile, compressive, flexural), matrix cracking, and delamination.

Fatigue

Fatigue damage in composites is thought to arise from non-reversible and micro-localized changes in composite structure under cyclic stresses or strains which increases in magnitude with increase in number of stress/strain cycles with damage manifesting initially as non-interactive cracks in the matrix and then progresses to fiber failure, interfacial debonding, and delamination as a saturation crack density is exceeded (Wu and Yao, 2010; Reifsnider *et al.*, 1983). Fatigue is a veritable source of damage to CFRPs and CFRP-metal joints as it is favored by the heterogeneity and anisotropy inherent in CFRPs and CFRP-metal joints which promotes dissimilar stress distributions (Wu and Yao, 2010; Barati *et al.*, 2019). The degradation of FRP due to fatigue is reportedly caused by the interaction of several damage types (Yao and Himmel, 2000). Since fatigue damage is a plausible source of damage for fiber reinforced composite structures, it is important to be able to detect, monitor, and predict fatigue damage and thus determine the remaining life-span of composite structures exposed to cyclic loads as with metallic structures. This is much easier for metallic structures but quite challenging for fiber reinforced composites due to among other factors the complex nature of the material properties which can vary significantly based on fiber layout/orientation and loading regimen, and consequent non-uniform damage development and non-elastic response of FRP during cyclic loading (Yao and Himmel, 2000). Damage to fiber reinforced composites can be described in a variety of ways; macroscopically and phenomenologically based on some changes/markers in material property such as fatigue modulus (Degrieck and Van Paepegem, 2001; Hwang and Han, 1986), secant modulus (Kennedy *et al.*, 2013; Talreja, 1987; Hahn, 1978; Hahn and Kim, 1976), residual strength (Hashin, 1985; Liu and Lessard, 1994; Chou and Croman, 1978), or compliance (Hahn and Hwang, 1982), and physically or microscopically based on some property related to the presentation of the damage such as density of cracks (Talreja, 1987; Hahn and Hwang, 1982), length of cracks (Spearing and Beaumont, 1992; Spearing *et al.*, 1992), delamination area (Takeda *et al.*, 1995, 1997; Ogihara *et al.*, 1999; Beaumont and Sekine, 2005; Bak *et al.*, 2014; Poursartip *et al.*, 1982, 1986; Poursartip and Beaumont, 1986), and number of broken fibers (Yao and Himmel, 2000; Wang and Chung, 1999, 1998, 1997). Generally, fatigue damage in composites can present as matrix failure, fiber-matrix interfacial debonding, fiber fracture, delamination, fiber micro-buckling, and void growth (Fig. 2) depending on the fatigue damage progression and conditions (Stinchcomb and Bakis, 1991; Corten, 1972; DorMohammadi *et al.*, 2017; Vassilopoulos, 2020; Gamstedt and Talreja, 1999; Alam *et al.*, 2019). Fatigue damage has been detected or monitored using a variety of techniques such as optical fiber sensors (Waite, 1990; Lee *et al.*, 2001; Liu *et al.*, 1996; Badcock and Fernando, 1995), thermoelastic stress analysis (TSA) (Shiozawa *et al.*, 2017), electrical resistance measurement (Wang and Chung, 1999, 1997; Gao *et al.*, 2010), Acoustic Emission Technique (AET) (Huang *et al.*, 1998; Kwon *et al.*, 2000; Kwon and Lee, 1999;

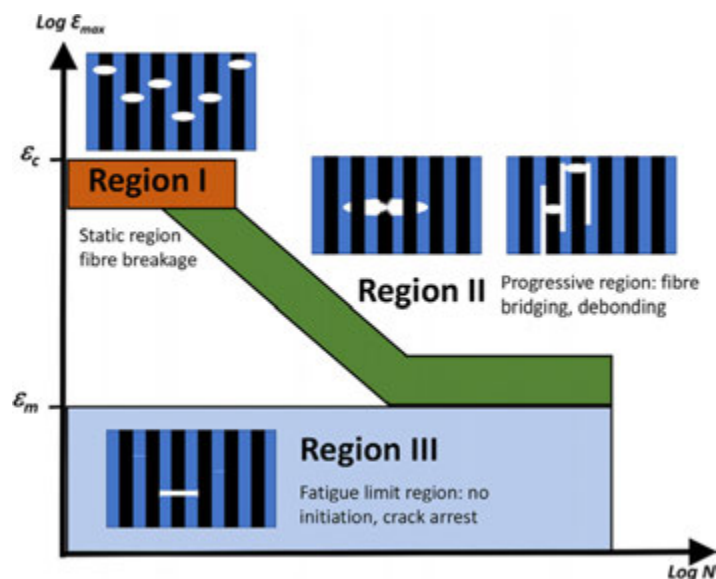


Fig. 2 Fatigue life diagram of longitudinal composites in tension-tension fatigue. Inspired by the work of Gamstedt, E.K., Talreja, R., 1999. Fatigue damage mechanisms in unidirectional carbon-fibre-reinforced plastics. *Journal of Materials Science* 34 (11), 2535–2546. doi:10.1023/A:1004684228765 and reproduced by permission of Elsevier from Alam, P., Mamalis, D., Robert, C., Floreani, C., Brádaigh, C.M.Ó., 2019. The fatigue of carbon fibre reinforced plastics – A review. *Composites Part B: Engineering* 166, 555–579. doi:10.1016/j.compositesb.2019.02.016.

Kwon and Kim, 1999; Tang *et al.*, 2017; Tang, 2019), X-ray Computed Tomography (CT) (Jespersen and Mikkelsen, 2016), Electro-Mechanical Impedance Spectroscopy (EMIS) (Miller and Hudak, 2020; Bois and Hochard, 2004; Soh and Lim, 2016; Loendersloot *et al.*, 2019; Lim and Soh, 2014; Malinowski *et al.*, 2014; Na and Baek, 2018), and impedance spectroscopy (Miller and Hudak, 2020; Lim and Soh, 2010; Pohl and Mook, 2010).

Creep

Creep is due to the viscoelastic flow/deformation of a material usually under (constant) load (Goertzen and Kessler, 2006). In fiber-reinforced composites creep can originate from straightening of uneven reinforcing fibers, viscoelastic deformation of the matrix, and/or creep of the reinforcing fibers (Oskouei and Taleie, 2010). Hence, creep properties of CFRP materials can result to stress redistribution in (hybrid) structural components comprised of CFRP, and thus exerts influences on the reliability and durability of such structures (Yang *et al.*, 2018; Ascione *et al.*, 2012; Braimah *et al.*, 2003). For CFRP composite tubes in the operating temperature range of 25°C to 100°C, Yang *et al.* (2018) had reported that creep rate increased with increasing applied stress and temperature, respectively. Consequently, high creep rupture strength and low creep coefficient(s) are desirable for enhanced creep resistance in fiber reinforced composite structures and CFRP-metal joints. Owing to its time-dependent nature, the creep behavior of fiber reinforced composites can be significantly affected by a variety of factors such as temperature, moisture, and mechanical loading (Scott *et al.*, 1995; Kim and Takemura, 2011). The presence of moisture is reported to affect creep properties of fiber reinforced polymers in a manner inferred to be consistent with moisture absorption triggered plasticization of the polymer matrix which manifests in lowered glass transition temperature of the polymer matrix (Scott *et al.*, 1995). Creep properties of fiber-reinforced composite materials can be measured by flexural creep tests (Goertzen and Kessler, 2006; Standard, 2004; Nuwayer and Newaz, 2018) and dynamic mechanical thermal analysis (Mohammadizadeh *et al.*, 2018; Bussu and Lazzeri, 2006).

Birur *et al.* (2006) studied creep induced failure of multi-directional fiber-reinforced polymer composites and concluded that creep failure of multidirectional polymer composite laminates is a complex phenomenon with contributions from a variety of damage modes quite similar to those observed for static overloading/failures; transverse (i.e., matrix) cracks, vertical cracks, delamination, splitting, and fiber fracture (Fig. 1). Since the presentation of damage due to creep is similar to that due to static failure, it stands to reason that spectroscopic techniques like EIS and EMIS can be employed to monitor progression of creep damage in fiber re-inforced polymer structures by periodic measurements over much longer time durations. Zhang *et al.* (2007) had reported that addition of single-walled carbon nanotubes (SWCNTs) in very low weight fractions (0.1%–0.25%) suppressed the load-induced reorientation of epoxy chains resulting in significant retardation of the creep response of the composite. Ghasemi *et al.* (2018) in their modeling studies of the creep behavior of carbon nanotube/fiber/polymer composite cylinders had concluded that addition of the multi-walled carbon nanotubes (MWCNTs) to the vinyl ester (matrix) is capable of reducing both the absolute values of the radial and circumferential creep strains, and the dimensionless effective stresses. Papageorgiou *et al.* (2019) studied the creep properties of poly (ether ether ketone) (PEEK) reinforced with graphene nanoplatelets (GNPs), (PEEK-GNP) and PEEK reinforced with a hybrid graphene/short carbon fiber (CF) filler (PEEK-CF-GNP) and reported reduction of both the creep deformation and recovery with increasing graphene nanoplatelets (GNPs) content which they attributed to enhanced creep resistance of the composites due to the addition of GNPs. Ayyagari and Al-Haik (2019) have reported that creep resistance of carbon fiber composites can be improved by incorporation of nanofillers (zinc oxide nanorods (ZnO) and carbon nanotubes (CNTs)) at the interface of carbon fiber laminae resulting in hybrid multiscale composites. These reports (Zhang *et al.*, 2007; Ghasemi *et al.*, 2018; Papageorgiou *et al.*, 2019; Ayyagari and Al-Haik, 2019) indicate that the use of hybrid multiscale fiber-reinforced composites by incorporation of “nanofillers” either in the matrix phase and/or in the interface between fiber and matrix is a plausible solution to improved creep response of fiber-reinforced composites.

Hygrothermal Effects

Hygrothermal effects in this work refers to the changes occurring in composites and/or composite-metal joints due to temperature and moisture or a combination of both. In CFRP composites hygrothermal effects predominantly affect the matrix, and increase in magnitude with increase in the temperature difference between the curing temperature and the operational temperature of polymer composite (Han and Drzal, 2003; Pethrick *et al.*, 1996; Lord and Dutta, 1988; Birger *et al.*, 1989; Budhe *et al.*, 2018). Starkova *et al.* (2013) reported that inclusion of nano-fillers into epoxy resins results in marked reduction in the diffusion coefficient of water in the composite which might be indicative of improvements in the barrier properties/resistance of the epoxy composite to water ingress. Zhou and Lucas (1999) studied the nature of water in epoxy resin (that comprise the matrix of many CFRP composites) at 45°C, 60°C, 75°C, and 90°C, for up to 1530 h and reported that water interacts with epoxy resin via 2 types of hydrogen bonding; Type I bonding with activation energy ≈ 10 kcal/mol, and Type II bonding with activation energy ≈ 15 kcal/mol. According to them (Zhou and Lucas, 1999), Type I bonding with lower activation energy involves a water molecule forming a single hydrogen bond with the epoxy resin network and hence are easier to remove as well as being the dominant presentation of much of the sorbed water. On the other hand, Type II bonding with higher activation energy involves a water molecule forming multiple hydrogen bonds with epoxy resin networks, and thus harder to remove, with its relative proportion in the epoxy strongly dependent on both the applied temperature and exposure time, and increasing as

both temperature and exposure time are increased (Zhou and Lucas, 1999). Hence hygrothermal effects in CFRP composites are most likely to be exacerbated by higher temperatures and exposure times.

Degradation due to hygrothermal effects arise mainly due to differences in both the moisture absorption capacities and the thermal expansivities and stabilities of the matrix and the reinforcing fibers which ultimately lead to internal stresses in the composite that are collectively referred to as hygrothermal stresses (Collings and Stone, 1985; Zafar *et al.*, 2012; Meng *et al.*, 2015). The presence of such stresses promote damage to the composite material under some service conditions and a consequent in reduction in mechanical properties (Zafar *et al.*, 2012; Ryan *et al.*, 2009; Apicella and Nicolais, 1985). In the presence of impressed polarization some of the water absorbed in the matrix of the carbon fiber reinforced polymer composite can yield reactive species (O_2^- , O_2^{2-} , OH^- , HO_2^-) (Ofogebu *et al.*, 2019a) that can promote ring opening reactions of the cured epoxy matrix for instance leading to concomitant chemical degradation of the matrix (Bao and Yee, 2002) in addition to damage due to internal stresses. In CFRP-metal joints under impressed polarization, the reactive species produced from breakdown of water adsorbed in the matrix and chemical products from ring-opening reactions of epoxy (e.g., amide/amine groups) of the matrix (Shin *et al.*, 2000a,b) can promote corrosion of the metallic members joined to the polymer composite. Such corrosion of metallic members joined to metal/polymer composites will result in formation of corrosion products on the metal surface which sabotages the integrity of the polymer composite-metal interface. Moisture and water uptake in epoxy/multi-wall carbon nanotube (MWCNT) composites have been reported to result in increase in electrical resistance under applied strain (Starkova *et al.*, 2015) which suggests that hygrothermal effects on composites might be monitored using electrical methods (Bekas and Paipetis, 2016; Du and Jana, 2008; Hübner *et al.*, 2019; Grammatikos *et al.*, 2018).

Galvanic Corrosion

Galvanic corrosion in the context of this work is accelerated corrosion (anodic dissolution) of metallic material(s) in electrical contact with CFRPs in the presence of moisture and oxygen due to electrochemical processes and/or the degradation of the CFRPs due to cathodic electrochemical processes. In the light of these, it can be inferred that most galvanic corrosion takes place in the presence of hygrothermal effects or hygrothermal damage. Hence it can be a challenge differentiating damage due to hygrothermal effects from that due to galvanic effects for CFRPs coupled to metallic material(s) under service conditions. The risk of galvanic corrosion is increased on joining conductive fiber reinforced polymer composites like carbon fiber reinforced polymers (CFRP) with metallic materials in multi-material assemblies in the presence of moisture (Ofogebu *et al.*, 2019a; Ofogebu, 2018; Santos *et al.*, 2015; Wang *et al.*, 2007b; Zhang *et al.*, 2017, 2019a; Mueller *et al.*, 2007; Tucker *et al.*, 1990; Bai *et al.*, 2014; Sloan and Talbot, 1992; Bauer *et al.*, 2018) with attendant deterioration of mechanical properties and structural integrity (Bauer *et al.*, 2018; Whitman *et al.*, 2017; Yang *et al.*, 2019). This risk of galvanic corrosion due to galvanic coupling of fiber reinforced polymers joined to metallic materials is further exacerbated by the emerging practice of enhancing the mechanical properties of fiber reinforced polymers by incorporation of nanofillers; many of which being conductive enhances the electrical conductivity of the polymer matrix (Ofogebu *et al.*, 2019a; Zhang *et al.*, 2013; Arronche *et al.*, 2013; Han *et al.*, 2017; Li *et al.*, 2019; Wang *et al.*, 2020a). Consequently, there is a need for better understanding of the plausible damage scenarios present in these multi-material systems in order to detect, monitor, and mitigate damage. Damage to carbon fiber reinforced polymer composites-metal assemblies present as damage to the polymer composites (principally at the matrix) due to operative electrochemical processes (Ofogebu *et al.*, 2019a; Ofogebu, 2018; Sloan and Talbot, 1992; Alias and Brown, 1992; Woo *et al.*, 1993; Faudree, 1991; Miriyala *et al.*, 1992), accelerated chemical degradation of the composite due to irreversible fracture of chemical bonds (Alias and Brown, 1992; Miriyala *et al.*, 1992; Zhang *et al.*, 2018; Yang *et al.*, 2012, 2014a), physical/chemical damage to the composite due to ingress of corrosive media/species (Sloan and Talbot, 1992; Zhang *et al.*, 2018; Tucker and Brown, 1989; Bellucci, 1992; Benmokrane *et al.*, 2007), accelerated corrosion of the metal(s) in contact with the composite (Ofogebu, 2018; Tavakkolizadeh and Saadatmanesh, 2001; Bellucci, 1991), and pH accelerated degradation (predominantly at alkaline pH) (Ofogebu, 2018; Yang *et al.*, 2014a; Sun *et al.*, 2016; Altamas *et al.*, 2015). Damage to CFRPs due to galvanic coupling to metals have been reported to manifest as blisters on the composite (graphite fiber/vinyl ester composite) (Tucker *et al.*, 1990; Alias and Brown, 1992; Tucker and Brown, 1989; Davis *et al.*, 1983), fiber/matrix interfacial breakdown (Ofogebu, 2018; Taylor, 1994; Taylor *et al.*, 1996; Kaushik *et al.*, 1991), matrix degradation (Ofogebu, 2018; Sloan and Talbot, 1992; Alias and Brown, 1992; Tang *et al.*, 2012), and erosion of reinforcing carbon fibers (Ofogebu, 2018).

Zhang *et al.* (2018) had reported that strong anodic and cathodic polarization of carbon fiber-reinforced composites could result in damage to their surface polymer layers. Such polarization induced damage to polymer surface layers can have adverse implications for structural integrity of composite-metal hybrid systems and polymer matrix-reinforcing fiber interfacial strengths (Zhang *et al.*, 2019a; Kim *et al.*, 2016; Zhang *et al.*, 2020). To mitigate the galvanic stimulated degradation of hybrid structures comprised of composites and metals a variety of strategies have been reported (Ofogebu, 2018; Edelstein *et al.*, 1996; Boyd and Hopper, 1997a,b, 1999; Boyd, 1995; Ofogebu *et al.*, 2019b; Mukesh and Hynes, 2019). A more detailed treatise on the intricacies involved in galvanically stimulated degradation of carbon fiber-reinforced composites and multi-material assemblies have been published elsewhere (Ofogebu *et al.*, 2019a). Acceptable solutions for monitoring and mitigating galvanically stimulated degradation in composites and/or composite-metal assemblies must; (1) not add significant weight to the structures, (2) not result in significant increase in total costs of the hybrid structure over its lifetime, and (3) not lead to significant reduction in the strength of the hybrid structures. In the light of these stringent requirements, a review of literature and patents related to mitigation of galvanically stimulated damage in composite-metal systems is presented.

Two classes of inhibitors; precipitation-based inhibitors like rare-earth acetates and nitrates (Ofogebu, 2018) and adsorption-based inhibitors like sodium dodecyl sulfate and azoles (Ofogebu, 2018; Ofogebu *et al.*, 2019b) have been identified to be able to reduce galvanic corrosion in CFRP-Al galvanic systems in aqueous media and/or on CFRP under simulated galvanic coupling conditions with metals, and found to exert some mitigative effects on polymer matrix degradation. Boyd (Boyd and Hopper, 1997a,b, 1999; Boyd, 1995) had reported the invention of a method for reducing both the galvanically stimulated degradation of conductive fiber reinforced composites and galvanic corrosion of metals that are electrically connected to these composites in multi-material assemblies by incorporation of an inorganic corrosion/degradation inhibitor into the polymer matrix. This approach can be classified as polymer matrix modification approach. Edelstein *et al.* (1996) reported a method for mitigating galvanic corrosion in carbon fiber-reinforced composite-metal systems based on modification of the reinforcing carbon fibers by intercalating carbon with compounds which might include oxidized forms of the metal(s). This method can be classified as a reinforcing fiber modification approach, and is premised on the claimed reduction of the driving force for galvanic reactions between the particles embedded in the reinforcing fibers and active metals in contact with the fibers and/or in aqueous environment. Srinivasan and Hihara (2016) had reported the use of hydrophobic coatings on insulative skirts to reduce galvanic corrosion between mechanically-fastened aluminum alloy and carbon-fiber reinforced polymer-matrix composites and attributed the results to disruption of the formation of a continuous electrolyte film.

Thermal Effects such as Overheating and/or Lightning Strike

In its diverse applications and service conditions such as in aircraft structures (Gardner, 2006; Segui, 2015; Katunin *et al.*, 2017a; Huang *et al.*, 2020; Katunin, 2016; Audiffred *et al.*, 2017; Martin *et al.*, 2017) and wind turbines (Yokoyama, 2013; Wang, 2016; Yasuda *et al.*, 2012; Vryonis *et al.*, 2016; Harrell *et al.*, 2017) carbon fiber reinforced polymers are prone to damage due to the sudden injection of large quantities of (electro-thermal) energy as is the case in lightening strikes. As a consequence there is a need to protect CFRP composites from damage in such scenarios. Recently, Wang *et al.* (2020b) sought to understand through experiments the mechanism of lightening induced damage in carbon reinforced polymer composites, and reported that damage due to lightening presented on CFRP surfaces as resin decomposition fiber breakage, fiber sublimation/vapourization, and ply-lift, but presents internally as delaminations. This report is consistent with reports on presentation of damage on CFRP due to lightening by other authors (Hirano *et al.*, 2010; Lee *et al.*, 2018; Feraboli and Miller, 2009; Li *et al.*, 2015b). Furthermore, they (Wang *et al.*, 2020b) concluded that damage to CFRP composites due to lightening is caused by the electro-thermo-mechanical response to lightning arc flow and Joule heating ablation resulting from the conductive nature of the CFRP composites.

Carbon fiber reinforced polymers (CFRPs) have emerged as multifunctional materials for which some degree of tuning in its properties might be beneficial in its varied technological applications to meet specific needs. Increased bulk conductivity of CFRPs is often an inadvertent consequence of efforts at improving the mechanical properties of carbon fiber reinforced polymers by incorporation of conductive nano-fillers like graphene and carbon nanotubes (Ofogebu *et al.*, 2019a; Miranda *et al.*, 2011; Lonjon *et al.*, 2012; Pozegic *et al.*, 2014; Pozegic *et al.*, 2016). Whereas the increased conductivity is a problem in combating galvanically stimulated damage of composite-metal assemblies (Ofogebu *et al.*, 2019a), it is desirable for mitigating damage due to lightening strike and thermal overloading (Katunin *et al.*, 2017a; Alemour *et al.*, 2019a; Hannemann *et al.*, 2016). Protection of carbon fiber reinforced polymers from lightening provoked thermal damage is hinged on improving the surface conductivity of carbon fiber reinforced polymers. The current and major industrial strategy employed to enhance the conductivity of CFRP composites in the aeronautical industry in order to mitigate damage from lightning strikes involves incorporation of meshes made of highly conductive metals (like copper and aluminum) into the composite (Gou *et al.*, 2010; Fisher and Plumer, 1977; Welch, 2007). However, this approach has disadvantages of increase in weight and complexity of composite structures, increased galvanic corrosion risks and consequent increase in maintenance costs (Alemour *et al.*, 2019a; Gagné and Theriault, 2014). Hannemann *et al.* (2016) reported that the electrical conductance of carbon fiber reinforced polymers can be enhanced by a factor of ≈ 30 by incorporation of highly conductive endless metal fibers into the carbon fiber reinforced polymers, and argued that this approach is feasible as elimination of additional weights for an electrical system compensates for the increased density of the composite. Other authors (Gou *et al.*, 2010; Han *et al.*, 2015; Shin and Kwon, 2011; Duongthipthewa *et al.*, 2017; Bollavaram *et al.*, 2018; Wang and Zhupanska, 2013; Alemour *et al.*, 2019b; Kumar *et al.*, 2019c; Dong *et al.*, 2017; Wang *et al.*, 2018a) have employed nanomaterials such as carbon nanotubes, carbon nanofibers, nano-particle-coated carbon fibers, carbon nanofiber paper, graphene nano-platelets (GnP) and carbon black nano-powders (CB) and metallic nanofilms, and use of conductive matrix resin (Katunin *et al.*, 2017a; Hirano *et al.*, 2016a,b). Damage to CFRPs due to lightning strikes and the consequent thermal overload presents principally as embrittlement (Gou *et al.*, 2010; Plumer and Robb, 1982), delamination (Gou *et al.*, 2010; Plumer and Robb, 1982), vapourization of resin in the immediate strike area (Feraboli and Miller, 2009; Li *et al.*, 2015b; Plumer and Robb, 1982), fiber breakup and blow up (Li *et al.*, 2015b; Hirano *et al.*, 2016b), and fiber pyrolysis (Feraboli and Miller, 2009; Li *et al.*, 2015b; Hirano *et al.*, 2016b). Besides the use of aluminum and copper meshes and expanded foils other methods for mitigating damage to CFRPs and CFRP-metal assemblies due to lightning strikes and the consequent thermal overload presents include; use of a conductive resin system for the matrix like polyaniline (Huang *et al.*, 2020; Hirano *et al.*, 2016b; Kumar *et al.*, 2019a,b, 2018; Katunin *et al.*, 2016, 2017b,c; Yokozeki *et al.*, 2015; Bhadra *et al.*, 2020), cold-spray deposition of conductive metallic layer on composite surface after prior creation of an electrochemically insulating layer on polymer composite surface (Bruton *et al.*, 2019), use of nickel coated carbon fiber nonwoven veils (Guo *et al.*, 2019), and use of electrically conducting polymer layer on structural

composite surface to circumvent issues of diminution of mechanical properties on blending non-conductive resins of the matrix with conductive resins (Manomaisantiphap *et al.*, 2020).

Sensing Material Degradation in different Composite Systems

According to Carden and Fanning (2004) damage identification can be classified into four levels: determination of presence of damage in a structure (Level 1), determination of the geometric location of damage (Level 2), quantification of the severity of damage (Level 3), and prediction of the outstanding service life of a structure (Level 4). In order to mitigate material degradation in practical applications it is necessary to be able to detect very early the onset of degradative effects. Effective strategies for sensing and monitoring damage will be dependent on the source of damage, the changes in the local environment due to the damage and/or changes in the local environment that provokes the damage or degradative effect, and the local changes in the composite in response to the stimulus (that is the presentation of the damage). Many conventional methods for damage monitoring, such as insertion of fiber optical sensors into the composite structure or attachment of piezoelectric sensors to the structure, are not quite suitable for smart protection of CFRP composites structures and CFRP-Metal joints due to high costs, poor durability, and possible sacrifice of some of the composite strength (Porfilio and Graziani, 2004; Wang *et al.*, 2005). Since in spite of the causes of the damage, damage in CFRP presents as discontinuities and/or localized changes in the electrical, optical and mechanical properties of the material, considering the need not to significantly add to the weight and cost of the composite or diminish its strength, the most viable option for smart monitoring and mitigation of damage in these systems would be exploitation of the composites local and global electrical properties. The electrical properties of conductive polymer composites have been exploited in the use of electrical techniques to monitor damage to conductive polymer composites which is based on the assumption that damage will result in reduction in measured conductivity values (Wang *et al.*, 2005; Schueler *et al.*, 2001; Todoroki *et al.*, 2002; Wang and Chung, 2007, 2006a,b; Wang *et al.*, 2006a,b; Chung, 2007, 2012, 2016, 2017, 2019; Wang and Chung, 2007; Shen *et al.*, 2007; Park *et al.*, 2015; Naghashpour and Van Hoa, 2015; Wen *et al.*, 2011; Kwon *et al.*, 2016; Gallo and Thostenson, 2015; Xi and Chung, 2020; Angelidis and Irving, 2007; Baltopoulos *et al.*, 2012; Haider, 2016). Recent trends (Jagt, 1998; Xu *et al.*, 2003; Sancaktar and Bai, 2011; Khoramishad and Razavi, 2014; Ashcroft *et al.*, 2000) indicating development of electrically conductive adhesive joints by incorporation of conductive nano-species increases the scope of usage of electrical methods to include monitoring of conductive adhesive joints.

In an interesting work Abry *et al.* (2001) monitored in-situ damage in CFRP using DC and AC electrical property measurements on the premise that electric resistance and capacitance changes can be correlated to changes in the conduction paths in the composite due to initiation and growth of damage in the composite. From their results they (Abry *et al.*, 2001) concluded that DC electrical conduction was sensitive to fiber failure, while AC measurements were more effective at detecting and monitoring matrix-related failures such as cracks, delaminations, fiber-matrix debonding or transverse cracks. These conclusions are important and needs to be highlighted as its exploitation can be quite beneficial to the development of smart damage sensing and protection systems for CFRP and CFRP-metal multi-material assemblies. In other works, the plausible efficacy of electrochemical impedance spectroscopy (EIS); an AC electrical property measuring technique in detecting and monitoring damage (particularly fiber/matrix interface damage (interfacial degradation of the carbon fiber and epoxy interface)) in carbon fiber-reinforced polymer composites in aqueous environments have been demonstrated (Ofoegbu *et al.*, 2019a; Ofoegbu, 2018; Taylor, 1994; Taylor *et al.*, 1996) and the particular utility/efficacy of the delta angle ($\Delta\theta$) measurements have been highlighted (Ofoegbu *et al.*, 2019a). Wang *et al.* (2006a) had reported that damage to composite materials due to fiber breakage and delamination results in increase of the measured electrical resistivity of the composites, while Wang and Zhupanska (2013) had reported that the electrical resistance measured at the bottom surface of the composite (along the fiber direction on the bottom surface) is the most sensitive to damage. The latter report is interesting as it suggests that it might be possible to monitor damage to a composite structure without accessing the damage site itself but by accessing the site opposite the damaged section, and thus increase the possibility of damage localization. In the light of these, we propose that the combination of spatially resolved DC electrical measurements and impedance spectroscopy offers a plausible solution for smart detection and monitoring of damage in carbon fiber-reinforced polymer composites without significant weight addition, dilution in strength and increase in cost of CFRP composite structures and CFRP-Metal joints (Figs. 2 and 3).

Current State of Art/Practice in Protection of Carbon-Reinforced Composite Materials and CFRP-Metal Joints

Materials whether they are metallic or non-metallic degrade on exposure to service environments. Hence the question; What is material protection? Material protection are steps taken to stop or reduce the rate of degradation of materials. The steps taken or steps that can be taken are dependent on the properties of the material to be protected, the service conditions, the source(s) of damage, the mechanism of damage, and consideration of the costs involved. Material protection systems or approaches can be either passive or active. In passive protection of materials, a protection scheme is put in place and is operative without regard to the commencement or non-commencement of material degradation events. In contrast, in active protection of materials the protection scheme is put in place but is only activated by damage to the structure to be protected and/or the on-set of degradative processes. Activation of damage mitigation process (or self-healing) in active protection can be designed to be triggered by any

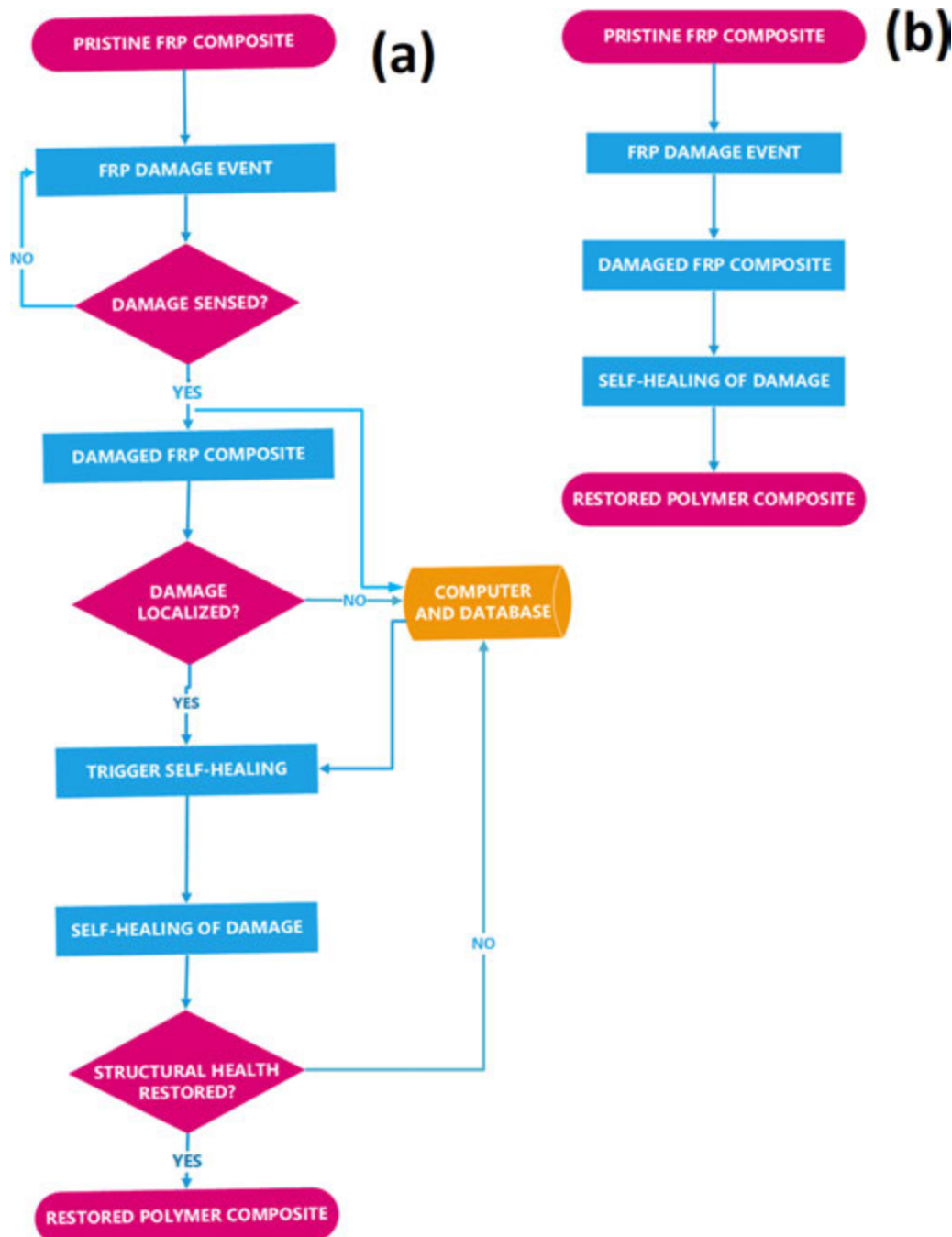


Fig. 3 Flowcharts for smart damage detection and protection of carbon fiber-reinforced composite structures (a) proposed flowchart, and (b) current flowchart similar to that used for smart coatings.

parameter which changes on damage to the structure to be protected or on on-set of degradative processes/reactions. Hence, generally speaking active protection can be considered to be synonymous with smart protection. A major benefit of smart protection of materials is the cost savings as protection is only activated when needed which elongates the time needed to renew the protection scheme(s).

Protection of a structure differs markedly from smart protection. Whereas protection of a structure can be expressed as actions and measures taken to maintain the functional integrity of a structure, smart protection refers to systems put in place so that a structure is able to autonomously or quasi-autonomously detect damage, and respond in such a way as to neutralize the damage and/or its effects, and recover its designed functional capabilities or a significant part of it. Current focus on smart protection of fiber-reinforced composites is principally based on imparting self-healing capabilities to principally the matrix phase (Chung, 2019; Yuan *et al.*, 2008; Blaiszik *et al.*, 2010; Bond *et al.*, 2008; Wu *et al.*, 2008; Naebe *et al.*, 2016; Wang *et al.*, 2015; Lee, 2020).

From literature reports (Chung, 2019; Hayes *et al.*, 2007b; Van der Zwaag *et al.*, 2014) four principal techniques have been identified to be in current use for imparting self-healing capability to composites. According to Chung (Chung, 2019), these techniques are encapsulation healing agents (in microcapsules, nano-capsules, microtubes, microfiber or nano-fiber shells, and microvascular channels) (White *et al.*, 2001; Kessler and White, 2001; Kessler *et al.*, 2003; Brown *et al.*, 2003; Brown *et al.*, 2002; Li *et al.*, 2015a; Muthu and Dendere, 2014; Aissa *et al.*, 2012; Blaiszik *et al.*, 2008; Hu *et al.*, 2014; Ghazali *et al.*, 2016; Bolimowski *et al.*, 2016; Vidinejevs and Aniskevich, 2017; Neisiany *et al.*, 2017a,b; Neisiany *et al.*, 2018; Wang *et al.*, 2016; Patrick *et al.*, 2014; Hamilton *et al.*, 2012; Hart *et al.*, 2017), remendable polymers (Wang *et al.*, 2007a; Kostopoulos *et al.*, 2016; Yang *et al.*, 2014b; Zhang *et al.*, 2016, 2014; Heo and Sodano, 2015), use of thermoplastic polymers (often thermally activated and without need for encapsulation) (Hayes *et al.*, 2007b; Pingkarawat *et al.*, 2012a,b, 2013; Jones *et al.*, 2015; Lim and Pickering, 2013; Lim and Pickering, 2014; Hayes *et al.*, 2007a; Meure *et al.*, 2009, 2010, 2012; Zako and Takano, 1999; Varley and van der Zwaag, 2008), and use of self-healing solvents (Celestine *et al.*, 2015; Caruso *et al.*, 2007, 2008; Manfredi *et al.*, 2014; Jones, 2015). The theoretical basis, intricacies and limitations of each of these techniques have been addressed in a recent review (Chung, 2019).

Application of Smart Protection Concept to Coatings for Mitigating Damage to Metallic Materials

Smart protection strategies have been developed for system comprised of metallic materials (Wang *et al.*, 2019; Shchukin *et al.*, 2016). Smart protection is an established and matured technology for coating applications. By a review of the design(s) and application(s) of the smart protection concept to coatings for mitigating damage to metallic materials, we aim to highlight the similarities and differences in requirements for smart protection of fiber-reinforced polymer composites and composite-metal joints, and thus identify the technology gaps that need to be addressed in order to realize smart protection for composite structures and composite-metal assemblies. Emphasis will be on the range sensing mechanisms which comprises the triggering stimuli and the designed stimuli response, and the consequent self-healing and repair.

In smart protection for coating applications the research/design emphasis seem to be on imparting the capability for autonomous interventions (Patrick *et al.*, 2016) like the release of corrosion inhibitors when needed to mitigate damage (active protection) to the substrate (metal) (Snihirova *et al.*, 2010; Shchukin *et al.*, 2008; Jakab and Scully, 2005; Tavandashti *et al.*, 2016; Qian *et al.*, 2019) and autonomous repair of the polymeric coating (self-healing) (White *et al.*, 2001; Wang *et al.*, 2017). This can be regarded as restoration of chemical/electrochemical degradation of substrate metal and restoration of the mechanical damage to the polymeric coating, respectively. Response to stimuli can be release of corrosion inhibitors from embedded microcapsules due to mechanical damage to the capsule coating or release of species that absorb/bind corrosive species in response to a trigger set off by corrosion processes such as changes in pH, metal ion concentration changes, etc. Recent reports (Wang *et al.*, 2019, 2017, 2018b) indicate efforts at imparting self-reporting capabilities (smart sensing) to anti-corrosive smart coatings so that they can be able to visually display the on-set of damage, progression of damage and the locale of the damage whether it is mechanical damage to the coating or corrosion damage to the metal substrate. Smart sensing (visual display) of the onset of corrosion damage had been achieved by use of fluorescent species (probes) that are sensitive to corrosion-initiated pH changes (Wang *et al.*, 2017, 2018b; Johnson and Agarwala, 1994; Augustyniak *et al.*, 2009; Maia *et al.*, 2013, 2014; Liu *et al.*, 2020a), while smart sensing capabilities for mechanic damage (which is more relevant to smart protection of FRP composites and FRP-metal joints) was obtained by using encapsulated fluorescent molecules that are liberated and/or transformed to visually perceptible forms due to mechanical damage to their containers and interaction(s) with the environment (Patrick *et al.*, 2016; Zheng *et al.*, 2020; Li *et al.*, 2016; Robb *et al.*, 2016; Guo *et al.*, 2016; Zhang *et al.*, 2019b; Michael *et al.*, 2015).

Kendig *et al.* (2003) exploited the energy of the corrosion process (polarization) to generate "on demand" a corrosion inhibitor that stops or reduces corrosion at defects by using anionic corrosion inhibitors as dopants in conducting (i.e., oxidized) polyaniline (PANI) films applied on an aluminum 2024-T3 substrate. On damage to the coating, anodic corrosion of the exposed metal provokes reduction of the doped PANI film which in its reduced state releases the inhibiting anions that mitigate anodic dissolution of the substrate metal. From this it is obvious that the energy from the damage event can be used to initiate and power the self-healing or repair process (smart protection). Possibility for application of similar approach to smart protection of composites is found in the contents of some reports (Fall, 2001; Kalista, 2003; Kalista and Ward, 2005, 2007; Kalista *et al.*, 2007; Varley, 2007; Kessler, 2007; Anonymous, 2004) which suggests that the heat energy generated on projectile impact with composites can be exploited to power self-healing/repair of damage to composites.

It is thus obvious that a smart protection system(s) for metallic materials (by use of active/smart coatings) needs to be capable of 2 major things; (a) detecting damage or its on-set, and (b) responding to the damage by releasing mitigating agents/species that act to annul the damage or stop the degradative processes. In contrast, a smart protection system suitable for fiber reinforced polymers (FRPs) and multi-material assemblies FRP-Metal joints must be capable of; (a) smart sensing/detection of damage, (b) localization of damage, (c) initiating damage mitigation/repair (self-healing) aimed at restoring structural integrity, (d) confirm damage is repaired and relevant structural integrity parameters are within range by comparison of parameter pre- and post-damage. From these requirements, it is obvious that a smart protection system for fiber reinforced polymers (FRPs) composites and multi-material assemblies FRP-Metal joints would need at least 2 key components that are not mandatory for smart protection of metallic materials using smart coatings; an extrinsic means of triggering self-healing capabilities (e.g., activation of a heat source, current source, etc.) and some signal processing/computational assets. In the light of these, some questions arise. Can smart protection systems developed for metallic systems be applied to carbon fiber reinforced polymers (CFRPs) and multi-material

assemblies (CFRP-Metal joints)? What are the similarities and differences in the degradation mechanism(s) in these different material systems? Can similar triggers (like changes in pH and met ion concentrations) employed in smart protection of metallic systems be exploited in smart protection of carbon fiber reinforced polymers and CFRP-Metal joints?

Smart Protection of Carbon-Reinforced Composite Materials and CFRP-Metal Joints

Self-sensing and self-healing capabilities in polymers though vital steps to smart protection of fiber-reinforced polymer composites does not strictly speaking constitute smart protection. These are actually vital components and desirable capabilities for development of smart protection strategies. The source of damage may not be as important as the presentation since in spite of the source(s) of damage the effects on the structure are similar and the design objective of a smart protection system to mitigate damage to composites is to detect damage and act in such a manner as to neutralize the consequent degradative effects on the structure. Smart protection of fiber-reinforced polymer composites would involve integration of self-sensing and self-healing capabilities with preferable inclusion of an external stimuli source when necessary and a feedback system. Currently, there is a dearth of reports (Garcia *et al.*, 2010; Hurley and Huston, 2011) on such protection system for fiber-reinforced polymer composites. Hillewaere and Du Prez (2015) identified and reviewed fifteen most important chemistries employed in autonomous external self-healing systems in which manual intervention(s) or additional stimulus is not required for the self-healing event to be achieved.

From the differences highlighted (Table 1) in the comparison of smart protection of metallic structures and fiber reinforced polymer composite structures, it is obvious that the methods and successes achieved in smart protection of metallic structures cannot be directly applied in smart protection of fiber reinforced polymer composite structures due to marked differences in materials involved, sites of damage, damage mechanism(s), and other damage related scenarios or indicators. Following the current trend of concomitant improvement of the electrical conductivity of fiber reinforced polymer composites in a bid to improve mechanical properties by addition of conductive nanofillers, an approach that fuls the need to detect and monitor damage without sacrificing mechanical properties or increasing weight and/or costs is most likely to involve exploitation of the electrical properties of reinforced polymer composites in a manner that the structure to be protected from damage becomes the damage sensor (intrinsic damage sensor). The most plausible approach to smart protection of composites and composite-metal assemblies/structures will depend on good understanding of electrical and electrochemical signatures of the various presentations of damage.

From the literature, it is obvious that there has been a lot of success in development of composite systems with self-healing capabilities (ability to respond to damage in a way to annul the effects) (White *et al.*, 2001; Pang and Bond, 2005a,b; Ullah *et al.*, 2016; Hia *et al.*, 2016). Hence the most vital missing link(s) in the trajectory for development of smart protection systems for reinforced polymer composite systems and composite-metal assemblies, is the ability to control and monitor the triggering of the self-healing step, non-destructive confirmation of restoration of structural integrity to acceptable limits, increase in damage-autonomous repair cycles and continuous monitoring of smart protected structures (structural health monitoring). Unlike in smart protective coatings where self-healing has been developed to be autonomous (i.e., without an external trigger), for fiber reinforced polymer composites exposed to some types of damage and/or operating conditions self-healing capabilities might have to depend on the introduction of an external stimuli (an external trigger) which is likely to increase the complexity of the smart protection system for these composites (Fig. 3). However, some success has been reported on autonomous self-healing of damage to fiber reinforced polymer composites (White *et al.*, 2001; Norris *et al.*, 2012). Van der Zwaag *et al.* (2014) reviewed current strategies to

Table 1 Differences in smart protection of metal corrosion/degradation and smart protection of composite degradation

<i>Fiber reinforced polymer composites</i>	<i>Corrosion/Coatings</i>	<i>Differences</i>
Degradation is not limited to composite surface hence smart protection is needed both on composite surface and inside fiber reinforced composite	Smart protection is needed mainly at the surface (i.e., interface between coating and metal substrate as corrosion is predominantly a surface phenomenon)	Differences in site for smart protection.
Degradation mitigating agent may need to be inserted in the matrix, at the interface between matrix and reinforcing fibers and/or inside reinforcing fibers	Degradation mitigating agents are inserted in the matrix of the inner coat of the smart coating system	Differences in sites for insertion of degradation mitigating agents.
Stresses due to variety of factors like overloading, thermal shocks, cracks. Matrix degradation due to ingress of moisture and in-situ generation of aggressive/reactive species (like O_2^- , O_2^{2-} , OH^- , HO_2^-) under service conditions.	Moisture, aggressive chemical species like Cl^- , and oxygen	Differences in factors necessary for degradation to commence.
Presence of cracks, loss of electrical continuity (reduction in conductivity), exposure to air or other activating agents due to release from cracked containers.	Changes in pH, ion concentrations, presence of moisture and cracks in coating.	Differences in stimuli needed to activate smart protection.
Main goal is restoration of structural integrity by restoration of mechanical properties.	Main goal is restoration of structural integrity by arresting electrochemical "dissolution" of substrate metal.	Differences in goal of smart protection

inducing self-healing behavior (smart protection) in fiber reinforced polymer-based composites, enumerated the challenges and concluded that although self-healing in fiber reinforced composites is a possibility it is unlikely to become a commercial reality in the near future. According to them (Van der Zwaag *et al.*, 2014) the challenges to development of a commercially successful self-healing system for fiber reinforced polymer composites are; (1) the optimized structure of current fiber reinforced polymer composites that leaves little “design space” for insertion of healing agent/reactions without loss of desired properties, (2) the chemical heterogeneity of fiber reinforced polymer composites, (3) presence of enormously large number of internal interfaces of diverse length scales and characteristics, and (4) marked diversity in the dimensions and topologies of damaged-induced crack in fiber reinforced polymer composites that demands case-specific optimization of any healing strategy.

With regards to in-situ damage sensing and localization that is vital for a smart protection system for fiber reinforced composites, we propose the use of impedance spectroscopy, a non-destructive technique that exploits the electrical properties of the composite as it does not require sensor to be implanted inside the composite. Several authors have reported (Gresil *et al.*, 2012; Bekas and Paipetis, 2016; Almuhammadi *et al.*, 2017; Baltzis *et al.*, 2017; Danoglidis *et al.*, 2019) its use for in-situ damage sensing in composite systems. Davis *et al.* (2002); Davis and Dacres (2001) had demonstrated the use of Electrochemical Impedance Spectroscopy (EIS) to monitor the health of adhesive bonds constructed from various combinations of aluminum, graphite/epoxy, glass/epoxy, glass/polyester, and glass/vinylester composites and reported that equivalent circuit parameters of the impedance spectra are sensitive to bond performance.

To improve the utility, accuracy and reliability of the smart protection system for fiber reinforced polymer composites proposed herein, it might be necessary to exploit the large data output via data mining tools and/or use of the large data output as training sets in artificial intelligence applications to better detect and respond to damage and/or predict damage trends. Due to the complexities in the composition of composites and marked variety in the presentation and evolution of damage in composites the use of machine learning (neural networks) had been proposed (Ofoegbu *et al.*, 2019a). Recently, Khan *et al.* (2019) presented a comprehensive review that dealt with damage assessment (detection, quantification, and localization) in composite structures using machine learning techniques and highlighted damage sensitive features for different types of damages in composite structures, and the corresponding optimal machine learning tools, which can be helpful in selecting appropriate combination of discriminative features and machine learning tools.

Conclusions

The use of fiber-reinforced polymer composites is increasing with applications in many sectors of the economy. With its deployment in critical infrastructure and environments and its unique anisotropy in mechanical properties and chemistry comes the need for early sensing and mitigation of damage. Hence smart protection system(s) for fiber-reinforced polymer composites with integrated damage sensing and self-healing capabilities and a feed-back system is a technological need. By a review of the trends in the development of smart protective coatings for protection of metallic substrates, the challenges to developing integrated smart protection systems for fiber-reinforced polymer composites and CFRP-metal joints are identified and some insight provided on the plausible research routes to accomplishing this task.

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Nanoporous Composites With Converse Magnetoelectric Effects for Energy-Efficient Applications

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Nomenclature

ALD Atomic layer deposition

BTO Barium titanate, BaTiO_3

CME Converse magnetoelectric effect

DME Direct magnetoelectric effect

EISA Evaporation induced self-assembly

FE Ferroelectric

FM Ferromagnetic

ME Magnetoelectric

MOKE Magneto-optic Kerr effect

PC Propylene carbonate

PMN-PT Lead magnesium niobate-lead titanate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$

PZT Lead zirconate titanate, $\text{Pb}[\text{Zr}_{(x)}\text{Ti}_{(1-x)}]\text{O}_3$

SQUID Superconducting quantum interference device

VSM Vibrating sample magnetometry

Glossary

Converse magnetoelectric effect Modulation of magnetic properties in magnetic materials by means of external electric field.

Direct magnetoelectric effect Modulation of electric polarization in dielectric materials by external magnetic fields.

Joule heating effect Energy dissipation induced by electrical currents flowing through a resistor.

Magnetoelectric composites Heterostructures which comprise magnetic and dielectric counterparts in which the properties of the magnetic material can be manipulated with voltage, either using solid or liquid electrolytes.

Magneto-ionics Magnetoelectric mechanism in which the oxidation state of the metal in the magnetic phase is

influenced by the ions (e.g., O^{2-}) diffusion back and/or forth from the material of interest toward an ion source/sink (e.g., a high O^{2-} mobility thin film, deposited next to the magnetic layer), depending on the voltage polarity.

Magnetostriction Ability of most ferromagnetic materials to expand or contract in response to an external magnetic field.

Single-phase multiferroics Materials possessing an inherent coupling between magnetic and electric orders.

Spinels A class of material, which crystallizes in the cubic crystal system, with general formula AB_2X_4 , where A and B are cations of (II) or (III) valent element (or the same element, as in Fe_3O_4) and X is an anion (typically oxygen or sulfur).

Introduction

Magnetism and electricity have always had an intimate link. Particularly interesting is the coexistence of magnetic and electric orders in magnetoelectric (ME) materials which makes them able to respond, simultaneously, to external magnetic and electric stimuli: (1) Electric polarization can be modulated by external magnetic fields (direct ME effect, DME) and (2) magnetic properties can be largely controlled with an electric field (converse ME effect, CME) (Wang *et al.*, 2010; Hu and Nan, 2019). In conventional ME composites, coupling between piezoelectric/ferroelectric (FE) and ferromagnetic (FM) constituents is mediated by strain and, in some cases, by electric charge effects (Wang *et al.*, 2010; Hu and Nan, 2019; Molinari *et al.*, 2019; Navarro-Senent *et al.*, 2019). In recent years, progress has been made in the so-called magneto-ionic heterostructures, where voltage-driven magnetic changes are mediated by ion migration/intercalation (typically O^{2-} , Li^+ (Dasgupta *et al.*, 2014; Zhang *et al.*, 2016) or H^+ species (Tan *et al.*, 2019)) (Bauer *et al.*, 2015; Duschek *et al.*, 2016; Gilbert *et al.*, 2016). DME effects are appealing for healthcare technologies (Chen *et al.*, 2017), water remediation systems (Mushtaq *et al.*, 2019a,b) and sensors/actuators (Wang *et al.*, 2010), whereas CME effects can be exploited in microelectromechanical systems and energy-efficient magnetic memories (Peng *et al.*, 2016).

Unfortunately, in FM films directly grown onto FE substrates, the voltage required to generate ME effects is extremely high (e.g., 4 kV) (Ahmad *et al.*, 2015) due to the large thickness of the substrate (i.e., in capacitors, electric field is inversely proportional to the dielectric thickness). This is not suitable for microelectronics, where much lower voltages (< 10 V) are desirable to enhance energy efficiency and not to burn the electronic components. If thin FE/FM bilayers directly grown onto rigid (non-FE) substrates, then the required voltages are lower, but the attainable strain is small due to the clamping with the substrate, thus also limiting the extent of ME effects (Torah *et al.*, 2004; Schmitz-Antoniak *et al.*, 2013; Chien *et al.*, 2016). To overcome these drawbacks, new ME composites based on nanoporous materials filled with either liquid or solid dielectric materials (eventually FE polymers) have been recently developed. These types of materials are overviewed in this article.

During the last two decades, much progress has been made in the synthetic procedures to prepare nanoporous systems with precise control of the porosity degree, pore/ligament sizes and crystallinity of the pore walls. This development has been triggered by the widespread use of these materials in chemistry areas such as catalysis, gas sensors, or supercapacitors, where a high surface-to-volume ratio (S/V) favors an enhanced performance. Also remarkable is the literature dealing with the growth and characterization of mesoporous composites containing embedded ferromagnetic particles, to be used in drug delivery applications (Trewyn *et al.*, 2007), ultra-light magnets (Heiligt *et al.*, 2014) or water remediation (Kharissova *et al.*, 2015). Interestingly, although many of the cutting-edge technological applications in nanomagnetism/spintronics also rely on surface or interface magnetic phenomena (e.g., spring-magnets, exchange bias, skyrmions, etc.) (Bibes *et al.*, 2011), the use of nanoporous materials in this field has been mainly overlooked.

In the particular subject of voltage-driven magnetic actuation, the study of nanoporous materials (i.e., mesoporous metals or oxides filled with a liquid high dielectric constant, or metal/metal oxide porous nanocomposites), all with high S/V ratio, is relatively new. In such materials, the relatively small effects from seminal works on magnetoelectric phenomena, initially observed in ultra-thin metallic films (Weisheit *et al.*, 2007), are drastically enhanced (Molinari *et al.*, 2018; Navarro-Senent *et al.*, 2019). In fact, it is easy to calculate that the S/V ratio of a 50-nm-thick porous film covering an area of $1 \times 1 \mu\text{m}^2$ and being made of a square array of vertically oriented cylindrical pores, with 5 nm pore diameter and 2.5 nm average pore wall (i.e., $\sim 50\%$ total porosity) is about 40 times larger than the S/V ratio of a fully dense layer of 50 nm thickness. Hence, the voltage-driven magnetic interfacial effects that depend on the S/V ratio (i.e., magnetic anisotropy, coercivity, direction of the magnetization, exchange bias), as well as those proportional to the total volume of affected material (e.g., the net magnetic moment) can be significantly enhanced in the porous architecture, by several orders of magnitude, with respect to non-porous magnetic thin films.

To measure the CME in nanoporous materials, either conventional magnetometry (vibrating sample or SQUID magnetometers) or magneto-optic Kerr effect techniques, in conjunction with custom-made setups to apply voltage, can be utilized (see Fig. 1). Either solid dielectrics (prepared by, e.g., atomic layer deposition) or liquid electrolytes, which form the so-called electric double layer upon voltage application, can be used.

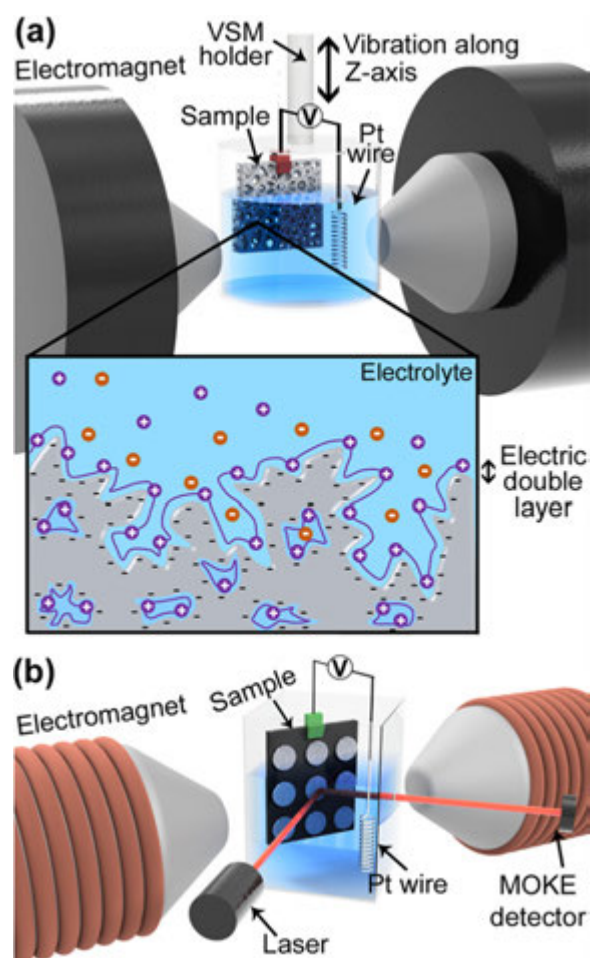


Fig. 1 Schematic illustration of the experimental setups typically used for magnetoelectric measurements in liquid configuration using (a) a vibrating sample magnetometer (VSM) and (b) a magneto-optic Kerr effect setup (MOKE).

The main body of this article is divided into three sections, covering CME in (1) metal-based composites, (2) metal/metal oxide systems and (3) all-oxide heterostructures, all based on nanoporous architectures. Here the use of the “composite” term is extended (as in the review paper by [Molinari et al., 2019](#)) to include those materials comprising a nanoporous framework filled with either a solid or a liquid second phase (often needed to generate the electric field or as buffer materials for magneto-ionics). We begin each section with a short introduction on the growth methods and experimental procedures used to induce and control the nanoporosity. We then focus on the most recent progress on the nanoporous ME composites belonging to each of the three categories, with emphasis on the systems where the ME effects are exacerbated due to the presence of nanoporosity. The article is followed by brief concluding remarks and perspectives.

Magnetoelectric Composites Based on Nanoporous Metals or Metal Alloys

Based on previous works on magnetism tuned by carrier density modulation in thin film magnetic semiconductors ([Ohno et al., 2000](#); [Chiba et al., 2003](#)), as well as preliminary theoretical works that predicted a strong dependence of the magnetic anisotropy energy on the number of valence band electrons in alloys such as Fe–Pt or Co–Pt ([Daalderop et al., 1991](#)), [Weisheit et al.](#) demonstrated in 2007 that the coercivity of ultra-thin Fe–Pt and Fe–Pd films could be modified by up to 4.5% under the action of external voltage during electrolyte gating ([Weisheit et al., 2007](#)). Since electric field in metals is confined within the Thomas–Fermi screening length (which is of the order of 0.5 nm), the changes in coercivity driven by voltage in metallic alloys were initially only observed in films of 2–3 nm in thickness.

In parallel to these works on ultra-thin metallic films, [Weissmüller et al.](#) showed that reversible changes in strain could be induced in nanoporous Pt due to electric surface charge accumulation ([Weissmüller et al., 2003](#)). Further investigations in that direction revealed that the magnetic susceptibility of nanoporous Pd ([Drings et al., 2006](#)) and the ferromagnetic properties of Pd–Co ([Ghosh et al., 2006](#)), Pd–Ni ([Ghosh, 2011, 2013](#)) and Au–Fe ([Mishra et al., 2010](#)) nanoporous alloys could be also manipulated with voltage due to these electrically induced variations of strain. In these works, the typical size of the crystallites comprised in the porous frameworks ranged between 8 and 20 nm. The charge-induced pressure on the nanocrystallites comprised in the nanoporous frameworks and the concomitant changes in sample dimensions during electrochemical charging and discharging processes were found to be responsible for these observations. In spite of their fundamental interest, the typical changes in magnetization due to strain effects are usually rather small (up to 0.5% at room temperature and 3% near the Curie temperature; [Ghosh et al., 2006](#)). An interesting theoretical work by [Subkow and Fähnle \(2011\)](#) analyzed in detail the effects of (1) filling of the electronic *d* band upon electric charging and (2) the magnetoelastic response to charge-induced strain variations in the nanoparticles forming nanoporous systems, both of which play a role during magnetoelectric actuation of these metallic alloys using liquid electrolytes. The authors concluded that the magnetic anisotropy energy of this type of systems can be modified with voltage only at the surface of nanoparticles (constituting the nanoporous framework) that are not in grain–boundary contact, which are the ones that can be effectively charged in the electrolyte due to the formation of the electric double layer when voltage is applied.

Subsequent works have been carried out to try to enhance the effects of voltage in the magnetic properties of nanoporous metallic alloys. Different experimental techniques have been used to improve the quality of the synthesized materials (i.e., to reduce the pore wall width or ligament size, or to make the porosity pseudo-ordered). Some of the most standard methods include micelle-assisted electrodeposition, electrochemical dealloying, or electrodeposition combined with colloidal templating (see [Fig. 2](#)).

Electrochemical dealloying is a method that allows fabricating porous films from previously deposited fully dense counterparts. In this case, the porous metal or metal alloy is obtained by selectively dissolving the most electrochemically active element comprised in an alloy. This technique has been shown successful to generate porosity in bulk metals, ribbons, as well as thin films (the latter grown by, e.g., electrodeposition or sputtering, as in the example shown in [Fig. 2\(a\)](#)) ([Sun et al., 2004](#); [Robbenolt et al., 2018](#)). Colloidal templating is a facile and cost-effective method to create well-defined, pseudo-ordered 3D porous structures by using 3D assembled nanospheres as a soft mask ([Dislaki et al., 2018](#)). Colloid size and self-assembly are factors that determine the nanopore dimensions, pore wall width and overall layer thickness (see [Fig. 2\(b\)](#)). Various methods to assemble monodisperse micro- and nanospheres have been put forward in the literature, such as dip coating, spin-coating, self-assembly, solvent evaporation, or electrophoresis. Among these methods, electrophoretic deposition is amongst the most attractive options for achieving homogeneous coverage of close-packed arrangements of spheres. Finally, micelle-assisted electrodeposition relies on the formation of micelles in the electrolytic bath which act as soft templates (structure-directing agents) during the growth of the metallic layers of interest. When a block co-polymer (e.g., P123) is added to the electrolyte at a concentration above “critical micelle concentration,” micelles start to form spontaneously in the solution, getting progressively in contact and tending to self-assemble at the solid–liquid interface ([Quintana et al., 2017](#); [Isarain-Chávez et al., 2018](#); [Li et al., 2018](#)). When voltage is applied to the cathode and reduction of the metal cations takes place, these micelles interfere and guide the electrodeposition process, leading to the growth of mesoporous metallic films (see [Fig. 2\(c\)](#)). The pore size (and pore wall size) is typically very small (even sub-5 nm). If the surfactant concentration is high enough to form a lyotropic liquid crystal, regular arrangements of pores can be obtained.

Remarkably, using this structure-optimized nanoporous alloys, changes up to 32% in coercivity (with virtually no significant variations in the saturation magnetization) have been reported in recent years in relatively thick films (0.5–1 μm) of various alloy compositions (nanoporous Cu–Ni, Co–Pt, Fe–Cu), mainly due to changes in the magnetic anisotropy energy stemming from electric surface charge accumulation, as evidenced by ab-initio calculations ([Quintana et al., 2017](#)). Depending on the alloy system,

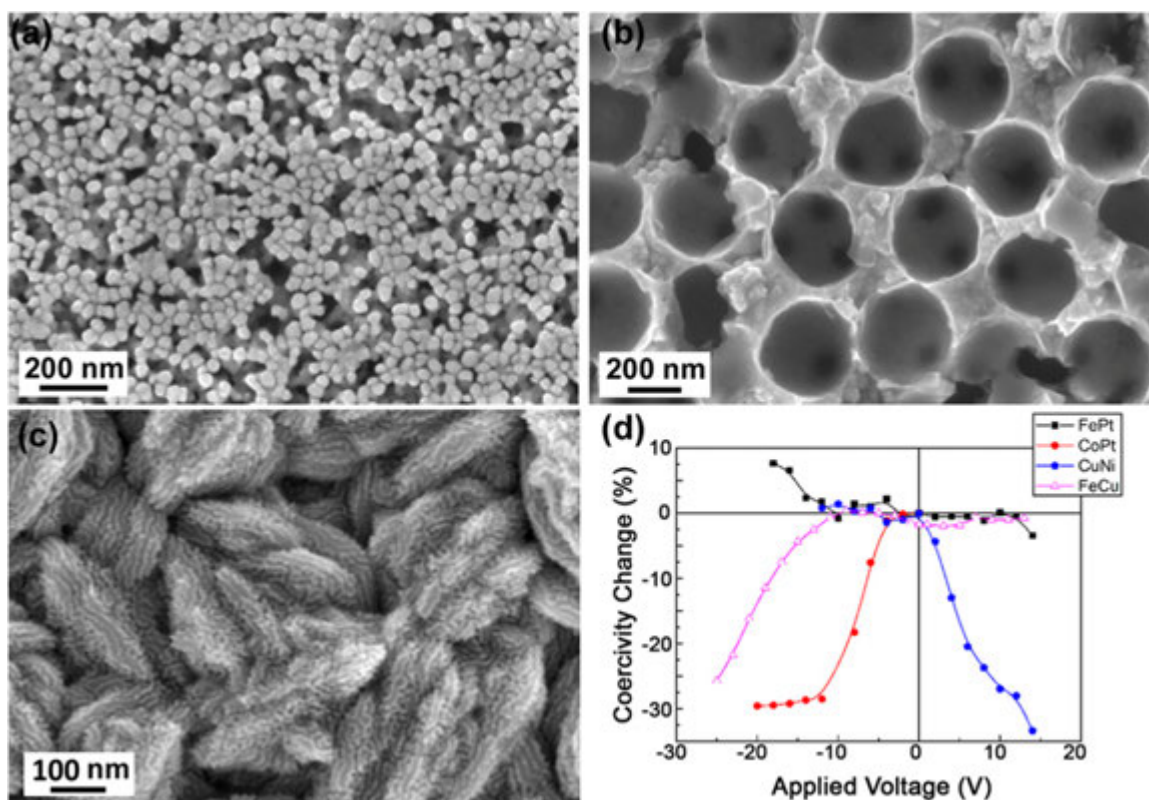


Fig. 2 Representative scanning electron microscopy (SEM) on-top images of (a) dealloyed Fe-Cu sputtered films, (b) electrodeposited Fe-Cu porous films grown onto colloidal templated substrates, (c) nanoporous Co-Pt films prepared by micelle-assisted electrodeposition. Panel (d) shows the relative variations of coercivity, as function of voltage, in various porous alloys electrolyte-gated using an anhydrous electrolyte (propylene carbonate). In all these cases, the voltage effects are mainly due to surface charge accumulation. Reprinted from (d) Navarro-Senent, C., Quintana, A., Menéndez, E., Pellicer, E., Sort, J., 2019. Electrolyte-gated magnetoelectric actuation: Phenomenology, materials, mechanisms, and prospective applications. *APL Materials* 7 (3), 030701. doi:10.1063/1.5080284.

the coercivity can either increase or decrease for either positive or negative applied voltages (Fig. 2(d)). Also, the changes in coercivity as a function of voltage polarity are often not symmetric. This can be due to the way the magnetic anisotropy energy varies with the electric field or because of the dissimilar thickness (and nature) of the electric double layer formed at the interfaces between the pore walls and the electrolyte during positive/negative voltage application. The experimental demonstration that the coercivity of thick nanoporous magnetic alloy films can be drastically reduced by simply subjecting this type of materials to the action of an electric field (i.e., applying a moderate DC voltage to them) is very appealing for energy-efficient magnetic actuation. If the coercivity is reduced, lower magnetic fields are needed to induce magnetization reversal (i.e., to write the magnetic bits of information in memory devices). As a consequence, less electric current is required, and this concurrently lowers undesirable Joule heating effects. The large S/V ratio and the ultra-narrow pore walls of these systems play a crucial role in the observed effects. Since electric field in metals is confined at their surface, the nanoporous morphology of the investigated materials allows for much larger accumulation of electrostatic charges compared to fully-dense films. That is, the whole nanoporous structure is affected by the electric field and not only the outer topmost surface, thus resulting in a very significant voltage-induced reduction of coercivity. This waives the stringent “ultrathin-film requirement” from previous studies, wherein smaller voltage-driven coercivity variations were reported (Weisheit *et al.*, 2007). Finally, besides coercivity, tuning of the superparamagnetic state has been achieved in nanoporous Co-Pd alloys electrically gated in a 1 M aqueous KOH electrolyte (Gößler *et al.*, 2019). The effect seems to be related to electrochemical hydrogen sorption. More specifically, a strong magneto-ionic (H^+) effect arises from coupling of the magnetic clusters via a Ruderman-Kittel-Kasuya-Yoshida-type interaction in the Pd matrix which is enhanced by the hydrogen sorption.

An overview of the different types of electrolytes, materials and main magnetolectric effects observed in nanoporous metallic alloys, metal/metal oxide composites and pure oxide systems is given in Table 1.

Magnetolectric Composites Based on Nanoporous Metal/Metal Oxide Heterostructures

In most of the examples discussed in the previous section, an anhydrous electrolyte (e.g., propylene carbonate) was utilized in order to induce electric charge accumulation at the surface of nanoporous metallic alloys (through the formation of the

Table 1 Representative materials, typical electrolytes and most prominent magnetoelectric effects induced in nanoporous materials with voltage (electrolyte-gating)

Electrolyte	Material	Variation	Reversibility	References
LiClO ₄ in EC	Nanoporous Au–Fe alloy	M = 0.2%	Yes	Mishra <i>et al.</i> (2010)
LiClO ₄ in EC	Nanoporous Pd–Ni alloy	M ≈ 0.5%	Partially (ΔV, ~1 h) Yes (ΔV, ~1 h)	Ghosh (2011)
PC	Nanoporous Cu–Ni film	H _C = –32%	–	Quintana <i>et al.</i> (2017)
PC	Pseudo-ordered porous Fe–Cu film	H _C = –25%	Partially (0 V, 5 min)	Dislaki <i>et al.</i> (2018)
LiClO ₄ in EC	Nanoporous Pd–Co alloy	M = 3%	Partially (ΔV, ~2 h)	Ghosh <i>et al.</i> (2006)
1 M KOH	Nanoporous Pd–Ni alloy	M = 24.6%	Yes (ΔV, ~2 h)	Ghosh (2013)
1 M KOH	Nanoporous Co–Pd alloy	M = 100% (ON–OFF)	Yes (ΔV, ~ h)	Göbller <i>et al.</i> (2019)
1 M NaOH	Nanoporous Cu–Ni	M _S = +33%	Yes (ΔV, 10 min)	Quintana <i>et al.</i> (2018a)
PC	Nanoporous Co–Pt lithographed disks	ΔM _S = 66% ΔH _C = –88%	Partially (DV, ~ min)	Navarro-Senent <i>et al.</i> (2018)
PC	Nanoporous Co–Pt + HfO ₂ /Al ₂ O ₃ films	Δm _S = 76% ΔH _C = –58%	Partially (ΔV, ~2 h)	Navarro-Senent <i>et al.</i> (2020)
1 M KOH	Porous γ-Fe ₂ O ₃ /Pt-nanocomposite	Δm = 10.4%	Yes (ΔV, ~5 min)	Topolovec <i>et al.</i> (2013)
LITFSI in EMIM-TFSI	Nanoporous Co _{0.5} Ni _{0.5} Fe ₂ O ₄ and CoFe ₂ O ₄ films	ΔM ≈ 2–5%	Yes (ΔV, ~ min)	Dubraja <i>et al.</i> (2018)
LITFSI in EMIM-TFSI	Nanoporous LiFe ₅ O ₈ films	ΔM ≈ 4%	Yes (ΔV, ~ h)	Reitz <i>et al.</i> (2016)
PC	Nanoporous Fe–Cu films	ΔM _S = 20% ΔH _C = 100%	Partially (ΔV, 40 min)	Robbenolt <i>et al.</i> (2018)
PC	Nanoporous CoFe ₂ O ₄ films	ΔM _S = 15% ΔH _C = +28%	Yes (ΔV, ~2 h)	Robbenolt <i>et al.</i> (2019a)
PC	Nanoporous CoFe ₂ O ₄ + HfO ₂ films	ΔM _S = +56% ΔH _C = +69%	Yes (ΔV, ~1 h)	Robbenolt <i>et al.</i> (2020)
PC	Nanoporous FeO _x films	ΔM _S = 1310% ΔH _C = +100%	Partially (ΔV, ~1 h)	Robbenolt <i>et al.</i> (2019b)

Abbreviation: EC, ethylene carbonate; EMIM-TFSI, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyle)imide; H_C, coercivity; LITFSI, lithium bis(trifluoromethanesulfonyl)imide; m, magnetic moment; M, magnetization; M_S, saturation magnetization; PC, propylene carbonate.

Note: Table adapted from Navarro-Senent, C., Quintana, A., Menéndez, E., Pellicer, E., Sort, J., 2019. Electrolyte-gated magnetoelectric actuation: Phenomenology, materials, mechanisms, and prospective applications. *APL Materials* 7 (3), 030701. doi:10.1063/1.5080284.

electric double layer). As aforementioned, this causes electric field induced changes in the magnetic properties (converse magnetoelectric effect), which are often reversible. In some cases, though, an aqueous electrolyte (e.g., 1 M KOH or NaOH) has been purposely utilized in the literature to trigger reduction–oxidation electrochemical reactions at the surface of the metallic porous frameworks or in metal/metal oxide islands when voltage is applied (Duschek *et al.*, 2018; Quintana *et al.*, 2018a). Sometimes, unexpected results have been encountered. For example, when positive voltage is applied to electro-deposited nanoporous Cu–Ni alloys and the films get oxidized, an increase (rather than a decrease) of the saturation magnetization is observed (Quintana *et al.*, 2018a). This counter-intuitive result can be understood because of the preference for Cu (rather than Ni) to get selectively oxidized. As a consequence, upon application of a positive voltage, the Cu–Ni alloy gets progressively enriched in Ni (as Cu is oxidized) and the resulting magnetic moment increases. The process can be fully reversed by application of a negative voltage. Oxygen migration can also cause changes in the coercivity of the nanoporous alloy, as well as in the perpendicular magnetic anisotropy (Ibrahim *et al.*, 2018). However, in nanoporous systems, since shape anisotropy is not clearly defined (i.e., these materials are typically polycrystalline and the ligaments and pore walls are randomly oriented), no pronounced anisotropy effects are typically reported.

Some nanocomposite porous materials contain oxide phases in the as-prepared states (as depicted in Fig. 3) (Navarro-Senent *et al.*, 2018; Robbenolt *et al.*, 2018). Some examples are nanoporous Co–Pt + CoO_x lithographed disks prepared by electrodeposition or nanoporous Fe–Cu + FeO_x + CuO_y films prepared by electrochemical dealloying. In these cases, migration of the structural oxygen (i.e., oxygen present in the as-prepared material) can occur when voltage is applied, even when utilizing anhydrous electrolytes, thereby rendering truly magneto-ionic effects (Navarro-Senent *et al.*, 2018). When this occurs, drastic changes in the coercivity and the magnetic moment at saturation take place. In some cases (e.g., nanoporous Fe–Cu solid solutions), this oxygen migration causes structural transformations in the metallic counterpart (e.g., from Cu-rich face centered cubic to Fe-rich body centered cubic phases) (Robbenolt *et al.*, 2018). Eventually, ON–OFF transitions (reversible transformations from ferromagnetic to paramagnetic or antiferromagnetic states) might be induced in nanoporous metal + metal oxide thin films, similar to what has been observed in nanostructured oxide thin films (Duschek *et al.*, 2018; Quintana *et al.*, 2018b).

Another effect that could be of interest in this type of nanocomposites would be the study of the eventual exchange bias phenomenon (i.e., shift of the hysteresis loop, along the magnetic field axis, due to the coupling between ferromagnetic and the electrochemically generated antiferromagnetic or ferrimagnetic phases). While this has been studied in flat, non-porous, multi-layered films (Gilbert *et al.*, 2016; Zhou *et al.*, 2016), comprehensive studies in nanoporous composites have not yet been reported.

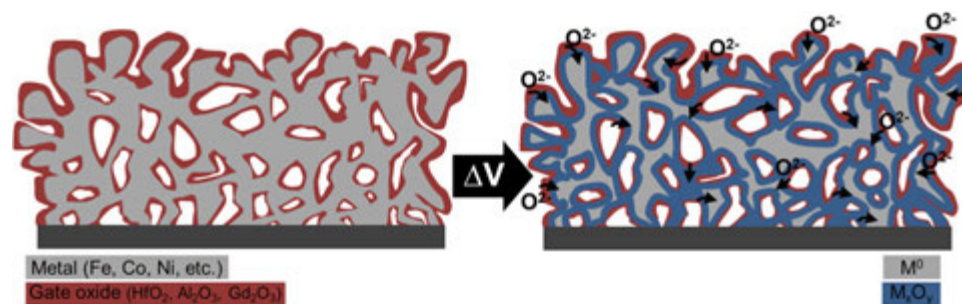


Fig. 3 Schematic drawing of voltage-induced oxygen migration in metal (M)/metal oxide (M_xO_y) magnetolectric composite under the action of an applied voltage, ΔV .

All-Oxide Nanoporous Magnetolectric Composites

Up to date, the vast majority of magnetolectric studies (in liquid and solid state) have been performed in oxide systems. As a matter of fact, all intrinsic multiferroics are oxides, for example, spinels (Fe_3O_4 , $CoFe_2O_4$), perovskites ($BiFeO_3$, $BaTiO_3$) (Liu and Yang, 2017) and hexagonal manganites ($RMnO_3$, where R is a rare-earth element) (Vaz *et al.*, 2010; Rao *et al.*, 2012). Furthermore, many oxides exhibit high magnetostriction coefficients ($CoFe_2O_4$, $La(Sr)MnO_3$) or high piezoelectric constants (PZT, PMN-PT, BTO) that makes them appealing for the design of various composite architectures where the magnetolectric effects are mediated by strain. Strain coupling requires an optimum mechanical matching between the two constituent phases, which is sometimes very difficult to achieve in ceramics. For this reason, the effects are only observed in epitaxial composite films or patterned structures where the crystallographic orientation and interfacial roughness are accurately controlled. Nevertheless, even in epitaxially grown composite films, the changes in magnetization induced by voltage are typically rather low ($< 5\%$), due to clamping effects with the substrate, which strongly limit the available strains.

Apart from the strain-mediated mechanism, an applied electric field can modulate the charge carrier density in oxide composite heterostructures, inducing noticeable changes in magnetization and coercivity. However, a direct demonstration of modulation of the magnetic properties in oxides heterostructures occurring through this mechanism remains relatively less explored (Schmitz-Antoniak *et al.*, 2013; Chu *et al.*, 2018). Furthermore, the presence of oxygen vacancies in the oxides has been shown to contribute to the magneto-ionic mechanism, where, as aforementioned, the voltage-driven oxygen ions migration can cause significant changes in coercivity, magnetization and magnetic anisotropy (Chien *et al.*, 2016). Various systems have been comprehensively analyzed and reviewed in recent articles (Song *et al.*, 2017; Chu *et al.*, 2018; Molinari *et al.*, 2019; Navarro-Senent *et al.*, 2019). In this section, we will focus specifically on the several oxide systems where the occurrence of nanoporosity has brought a significant contribution to the observed ME effects: Multiferroic $BiFeO_3$, solid state $CoFe_2O_4$ /PZT, solid/liquid $CoFe_2O_4$ /PC, and FeO_x /PC composites, and lithiated spinel ferrites.

The synthesis of the nanoporous oxides traditionally relies on the evaporation induced self-assembly (EISA) of the sol-gel type inorganic precursors and the amphiphilic diblock co-polymer templates, as depicted in Fig. 4. In aqueous or organic solvents, the precursors (e.g., metal chloride or nitrate) are hydrolysed and condensed to form inorganic polymers composed of M–O–M bonds (M is the metal). At the same time, the polymer forms micelles which attach to the metal ions (Step 1). During the dip-coating process, the polymer and sol-gel precursors are progressively concentrated by evaporation, leading to aggregation, gelation, and final drying to form a type of dry gel layer (Step 2). As a final step, the layers are heated in a controlled atmosphere in order to crystallize the oxide and burn out the polymer template which leaves behind the porous structure (Step 3). Remarkably, the nanoporous films can be also obtained directly by dip-coating, without the use of the polymer template (Robbenolt *et al.*, 2019b). In this case the degree of nanoporosity is governed by the solvent evaporation rate. A representative image of the FeO_x film produced by dip-coating in the absence of polymer template is also given in Fig. 4. This is a simple and relatively fast method to grow nanoporous oxide films with the controlled thickness, porosity and crystalline structure. More details on the methodology and the effect of the synthesis parameters can be found elsewhere (Schneller *et al.*, 2013; Zhang *et al.*, 2019; Galy *et al.*, 2020).

The mechanical flexibility brought by nanoporosity can provide a powerful tool to strain engineer nanostructured materials (Quickel *et al.*, 2010). The studies performed on internal multiferroic $BiFeO_3$ (Quickel *et al.*, 2015) revealed that the voltage-induced change in d spacing was 10 times greater than in the dense film of the same composition. However, it is not only the extent of the lattice strain that matters, but also the nature of strain. As the material is clamped to a rigid substrate, there is a gradient of strain (anisotropic strain) developed during the application of electric field. The strain symmetry lowering appears to be the key to the observed amplified voltage-induced magnetization of $BiFeO_3$, which exceeds the one of epitaxial $BiFeO_3$ systems. Indeed, the numerical results are impressive: upon electric field application the material shows a large change in saturation magnetization, from 0.04 to 0.84 μ_B per Fe, which is > 20 times higher than in the dense sample.

This seminal work by Quickel *et al.*, paved a way towards the use of flexible nanoporous architectures for strain engineered ME composite materials. The later reports, where the pores are employed as a host to accommodate dielectric compounds, have proved the importance of nanoporosity for strain-engineered oxide systems. Nanoporous $CoFe_2O_4$ was produced using polymer templating of sol-gel derived thin films, followed by conformal filling the pores with a piezoelectric $Pb(Zr,Ti)O_3$ using atomic

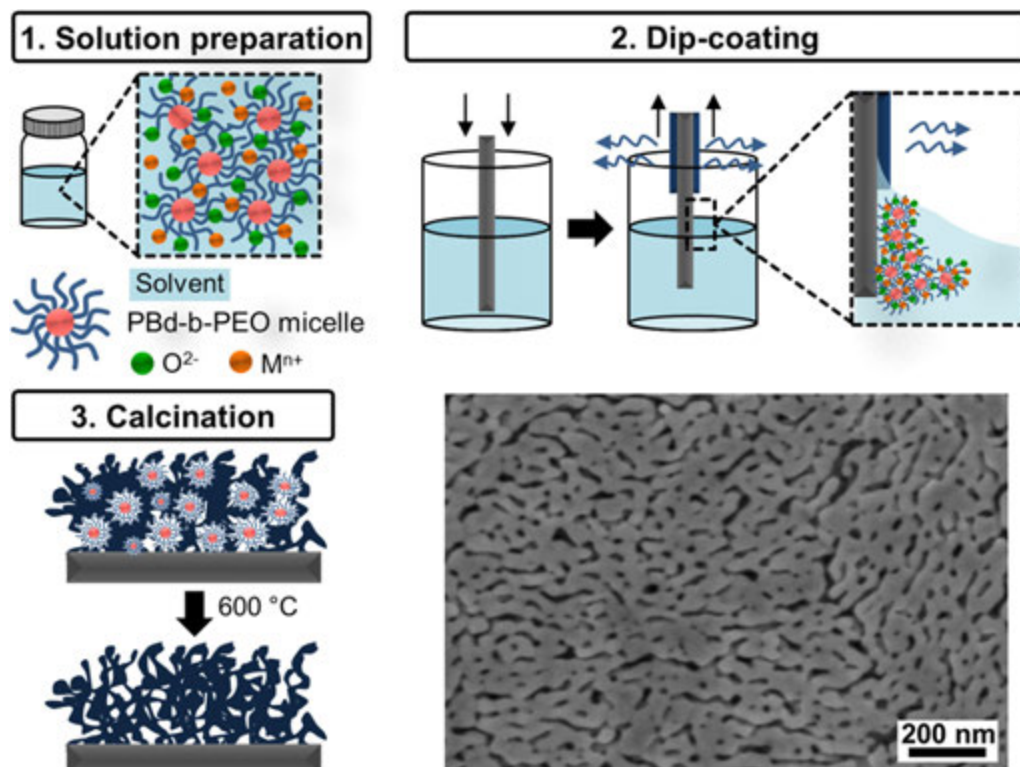


Fig. 4 Schematic pictures of the template-assisted sol-gel process used to induce nanoporosity in oxide films and a representative SEM image of nanoporous FeO_x layer obtained after calcination.

layer deposition, which resulted in a solid state composite ME material with a very high interfacial area (Chien *et al.*, 2016). Both materials are well documented in the literature and have generated significant interest due to their ferroic properties (Schmitz-Antoniak *et al.*, 2013; Rodzinski *et al.*, 2016; Paudel *et al.*, 2019). However, previous studies were focused on dense films where the magnetoelectric effects are significantly limited by substrate clamping and the effects of nanoporosity were mainly overlooked. In porous CoFe_3O_4 films grown on rigid substrates, the bottom of the layer remains clamped and therefore the in-plane strain is hindered. Nevertheless, the nanoporosity allows for out-of-plane flexing and thus, for more bond distortion in both $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and in the coupled CoFe_3O_4 as compared to dense films. Indeed, with the application of positive voltage, the most pronounced change in saturation magnetization was measured along the perpendicular-to-plane direction, that is, M_s increases by 15.4% (compared to 3.6% for in-plane measurements). Remarkably, the observed ME effects are reduced when the thickness of the $\text{Pb}(\text{Zr,Ti})\text{O}_3$ increases. This again underscores the importance of the mechanical flexibility of the nanoporous frameworks, as thicker piezoelectric layer seals the pores, thus lowering the mechanical distortion and the strain transfer. However, the voltage-induced strain in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ is lost when the driving electric field is removed, that is, the observed effects are rather volatile.

Non-volatile, fully reversible electric-field control of magnetism in nanoporous CoFe_3O_4 was achieved by magneto-ionic means, where a liquid electrolyte (propylene carbonate treated with metallic Na) was used to access the open porosity of the material (Robbenolt *et al.*, 2019a). Applying moderate negative voltage to the sample, between -10 and -50 V, causes a partial reduction of metal ions to zero valent state ($\text{Co}^{2+} \rightarrow \text{Co}^0$ and $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} \rightarrow \text{Fe}^0$) which is accompanied with the oxygen ions migration towards the surface or/and out of the sample. This leads to a maximum increase of M_s by 15% (see Fig. 5) and a decrease in H_C by 28% in the porous sample after applying -50 V. Analogous samples with lower porosity degree (synthesized by dip coating but without the diblock co-polymer) exhibit more modest magneto-ionic effects, that is, 2% increase in M_s and 4% decrease in H_C . This underscores the importance of nanoporosity in this system. The oxygen ion exchange between the sample and the liquid electrolyte occurs mainly at the solid/liquid interface, thus there are two main contributions from nanoporosity: (1) an enhanced overall interface area and (2) larger electric fields due to the reduced size of the ligaments (reduction of the effective thickness of the film since the electrolyte can penetrate towards the interior of the pores).

The way the oxygen ions are stored appears to be the key factor determining the reversibility of the magnetoelectric process. It has been demonstrated that the O^{2-} can be either dissolved in the electrolyte (Quintana *et al.*, 2018b; Robbenolt *et al.*, 2018) or aggregated at the grain boundaries forming oxides/hydroxides. In the case described above, that is, $\text{CoFe}_3\text{O}_4/\text{PC}$, the migratory oxygen was likely stored at the surface or at the grain boundaries which made it easier to reincorporate it back into the cobalt ferrite structure with the voltage of opposite polarity (Robbenolt *et al.*, 2019a). Indeed, a similar study performed on nanoporous FeO_x immersed in a liquid electrolyte demonstrated that the voltage-induced changes in M_s can be only partially reversed in the nanoporous sample when the oxygen ions are stored in the solution (Robbenolt *et al.*, 2019b). The O^{2-} ions can be stabilized by

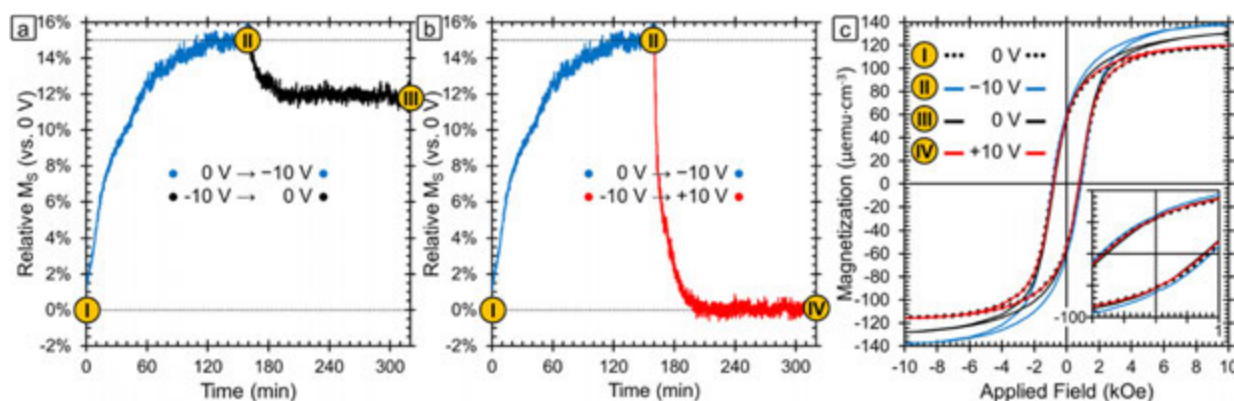


Fig. 5 (a) Relative change in saturation magnetization (M_S) vs. the initial sample magnetization as a function of time and applied voltage for nanoporous CoFe_2O_4 films. Point I is the initial sample as-synthesized. The blue line shows the evolution of the magnetization during the application of -10 V for 160 min and point II is the maximum magnetization reached. After the application of -10 V, the voltage was turned to 0 V (black line) in one case and $+10$ V (red line) in another, as it is shown in panel (b). Points III and IV are the sample state after the sample relaxed at 0 V and recovered under $+10$ V respectively. (c) Room-temperature magnetic hysteresis loops corresponding to points I–IV. The figure is reprinted from Robbenolt, S., Menéndez, E., Quintana, A., *et al.*, 2019a. Reversible, electric-field induced magneto-ionic control of magnetism in mesoporous cobalt ferrite thin films. *Scientific Reports* 9, 10804. doi:10.1038/s41598-019-46618-6.

polar solvent molecules and, depending on the voltage intensity, these ions remain in the electrolyte or become neutralized at the counter-electrode. In the latter case, the overall system loses part of the oxygen in form of bubbles which can make the magnetolectric changes fully irreversible. In this case, the ability of the system to be re-oxidized will be dictated by the diffusion kinetics of the process.

Recently, magneto-ionic effects in spinel oxides have attracted the attention of scientists working on lithium ion batteries. Such materials (LiFe_5O_8 , CoFe_2O_4 , NiFe_2O_4 , etc.) show ability to reversibly incorporate Li^+ ions from a liquid electrolyte and subsequently release these ions in a specific range of applied voltage (Reitz *et al.*, 2016; Dubraja *et al.*, 2018). Lithium intercalation causes a valence change and a partial redistribution of metal cations in the spinel structure, hence resulting in a large increase in magnetization at room temperature, that can be as high as 30% in some cases (Dasgupta *et al.*, 2014). Remarkably, magnetization reversal dictated by lithium intercalation mechanism is highly reversible (endurance of thousands of cycles), although only to a certain degree of lithiation, beyond which the original spinel structure cannot be fully recovered anymore. This is in line with the other works on oxides discussed previously in this article. Furthermore, the highly porous structure of these oxides allows for a reduced diffusion distance, while enhancing, to some extent, the mechanical resistivity of the material against failure due to volume changes (electrode breathing) during lithiation/de-lithiation.

Challenges and Perspectives

In recent years, exciting new results in the field of magnetolectric actuation have been obtained in composites comprising metallic, semiconducting and dielectric nanoporous structures. The presence of nanoporosity allows for significant changes in the magnetic properties under application of moderate voltages. Furthermore, such systems are able to outperform at room temperature, compared to fully dense films with the same composition. This eventually leads to reduced energy cost and facile integration of these materials into devices. Indeed, there is a huge potential for these systems to be utilized in a myriad of energy-efficient applications: spintronic devices, energy harvesters, radio-frequency/microwave devices, non-invasive biomedical technologies, and neuromorphic computing platforms (Hu and Nan, 2019; Mishra *et al.*, 2019). Nevertheless, in most cases, the use of a liquid electrolyte is required to generate ultra-high electric fields (thanks to the formation of ultra-narrow electric double layers) and to access the large surface area of the complex 3D nanoporous networks (Navarro-Senent *et al.*, 2019). For further technological exploitation of these enhanced magnetolectric effects it is important to fully adapt ME composites to operate in solid state. In fact, the pores can accommodate various host FE materials that can conformally coat the overall surface of highly porous FM phases, thus resulting in a new type of composite materials able to operate in all-solid state via magneto-ionic, strain-mediated or charge accumulation mechanisms, depending on the nature of the FM/FE materials. Particularly, there is large potential for nanoporous materials to be integrated in strain-mediated composites, for example, filling the pores with FE polymers to take advantage of the synergies between magnetostriction and piezoelectricity (e.g., PDVF (Martins *et al.*, 2015; Poddar *et al.*, 2018)), analogous to bioinspired three-dimensional magnetoactive scaffolds (Fernandes *et al.*, 2019). In addition, magneto-ionic control of magnetism can be achieved in nanoporous ME composites, where the guest material can be a solid electrolyte (ionic conductor) grown throughout the surface of the porous framework using, for example, ALD such as a high O^{2-} mobility thin film like Gd_2O_3 .

or HfO_2 (Detavernier *et al.*, 2011). In fact, it has been recently demonstrated that larger magneto-ionic effects can be obtained in nanoporous cobalt ferrite film conformally coated with HfO_2 , as compared to a film having the same degree of porosity but simply immersed in an anhydrous electrolyte (Robbenolt *et al.*, 2020). Nevertheless, in this case, a liquid electrolyte was still employed during voltage application to avoid the problem of electrical pinholes in HfO_2 . Furthermore, the magneto-ionic speed needs to be further increased, while keeping the reversibility and cyclability of the effects at room temperature. This challenge is being tackled by using hydrogen magneto-ionics instead of oxygen (Tan *et al.*, 2019), or optimizing the electric contacts and sample designs (de Rojas *et al.*, 2020). However, in spite of all these works, the mechanisms responsible for magnetoelectric actuation are, in general, still rather poorly understood.

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Magnetocaloric Composite Materials

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Nomenclature

H Magnetic field

H_f Final magnetic field

H_i Initial magnetic field

η Parameter used in Bean and Rodbell model to govern the order type of phase transition

M Magnetization

n Exponent governing the magnetic field dependence of ΔS_{iso}

RC Refrigerant capacity

RCP Relative cooling power

S_M Magnetic Entropy

ΔS_{iso} Isothermal entropy change

T Temperature

ΔT_{ad} Adiabatic temperature change

T_C Curie temperature

T_{lift} Temperature span used for the calculation of TEC

T_{span} Temperature span

TEC Temperature averaged entropy change

Glossary

First order phase transition A phase transition that involves a discontinuity in the first derivative of free energy with respect to a thermodynamic variable.

Magnetocaloric effect Reversible temperature change of a magnetic material due to the change of the magnetic field that it experiences.

Refrigerant capacity Amount of energy that can be transferred between the hot and cold reservoirs in a refrigeration system.

Regenerator bed Part of the magnetocaloric refrigerator that contains the magnetocaloric material.

Second order phase transition Also known as continuous phase transition, a phase transition with continuous first derivatives of free energy but discontinuous second derivatives. It can be described using scaling laws and critical exponents.

Introduction

Energy-efficient cooling technology is extremely important in today's society as our lifestyle largely depends on controlling the temperature of the places where we live and work and of the food that we will eat. This has to be performed while keeping in mind the need for conserving energy and mitigating global warming. Magnetic refrigeration (MR), one of such cooling technologies, utilizes the magnetocaloric effect (MCE), which enables quieter and better energy efficiency compared to the conventional gas-compression refrigeration. Furthermore, it eliminates the use of harmful and hazardous refrigerants, such as ozone-depletion or greenhouse gases, making MR an environmental-friendly alternative to conventional refrigeration. There is a broad variety of magnetocaloric materials that have been studied to date, with various characterization and alloy preparation techniques recently reviewed by Franco *et al.* (2018). Rather than abounding in the most mainstream single-phase materials, this article focuses on the current state-of-the-art of magnetocaloric composites, highlighting the motivation of their development and their performance. Various analysis methods related to studying the MCE of composites and their phase deconvolution will also be reviewed. Even though MCE is not yet in the consumer market, we will share our opinions about how magnetocaloric composite materials might develop with the use of upcoming additive manufacturing and with combination of different functionality.

The Magnetocaloric Effect: Fundamentals

The magnetocaloric effect (MCE) describes the reversible temperature variation of a magnetic material when it is adiabatically magnetized or demagnetized. This engages the manipulation of the degrees of freedom of the magnetic sub-system with the variation of a magnetic field and their coupling to the degrees of freedom associated to the structure/lattice, thereby considering MCE as an intrinsic phenomenon in magnetic materials. By using appropriate cycles, the transfer of energy between these two subsystems can be used for magnetic refrigeration, with Fig. 1 schematically illustrating one of such cycles based on the MCE: Upon the adiabatic application of an external magnetic field, the magnetic moments align parallel to the field, which then decreases the magnetic component of the entropy ($a \rightarrow b$). As a result, the lattice entropy increases since the total change in entropy in an adiabatic process remains as zero, leading to an induced increase in the temperature of the material (Fig. 1(b)). This extra heat can be easily expelled to the environment ($b \rightarrow c$) using a heat-transfer medium, such as water, a gas or another fluid passing

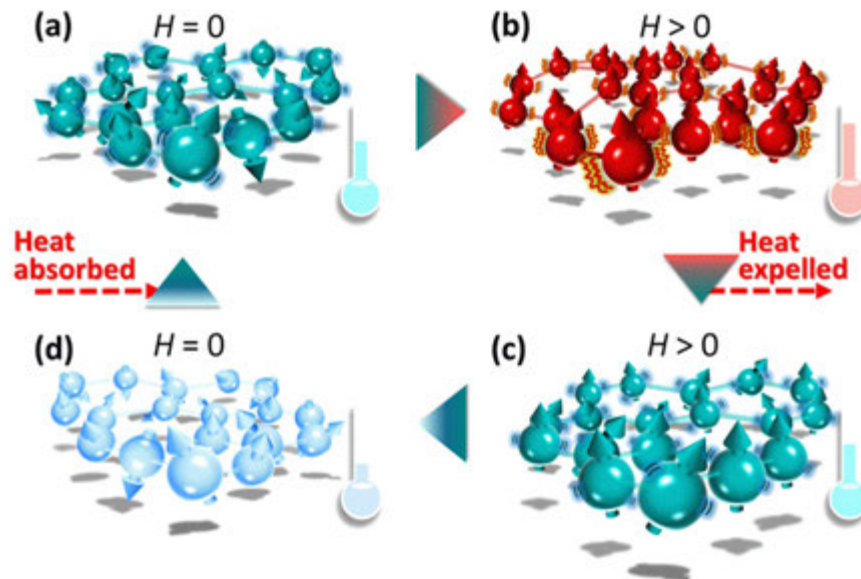


Fig. 1 Schematic representation of a magnetic refrigeration cycle: magnetocaloric material heats up upon adiabatic magnetization (a→b); the excess heat previously induced gets ejected from the material by a heat transfer fluid (b→c), cooling down the material (c) back to the initial temperature in (a); it further cools down upon adiabatic demagnetization (c→d) and can thus be utilized to cool the load (refrigerator).

through the magnetocaloric material. During adiabatic demagnetization (c→d), the magnetic material cools (i.e., an adiabatic temperature change) due to the increase in the disorder of the magnetic moments, which results in lower lattice entropy. In this case, heat can be extracted from another chamber (from inside the refrigerator or the room whose temperature we want to control) to the material by placing it in thermal contact with the (heat) load where its temperature increases and it acts like a refrigerant. As the material regains its thermal equilibrium, i.e., back to the initial temperature in (a), it could undergo the same process again, making it as a reversible cycle. This description applies to conventional MCE (i.e., materials whose equilibrium magnetization decreases with temperature) while the inverse effect would bring upon lower temperatures during adiabatic magnetization for materials whose magnetization increases with increasing temperature, such as during antiferromagnetic-ferromagnetic phase transitions.

Therefore, one can imagine that a large MCE is obtained with a large change in the order of the magnetic subsystem, which happens in the vicinity of the Curie transition of a ferromagnetic material (also applicable to other type of magnetic transitions). This also brings upon a reduction in the magnetic entropy of the system (S_M), where in a reversible process, isothermal demagnetization restores the zero-field S_M , thus quantifying MCE as an isothermal entropy change, ΔS_{iso} . This is depicted in **Fig. 2(a)** where the maximum ΔS_{iso} is observed near the magnetic phase transition of the material (e.g., Curie temperature (T_C)). Furthermore, this ΔS_{iso} inflicts a change in vibrational lattice entropy (e.g., the latter increases during adiabatic magnetization in a reversible process in **Fig. 1(b)**), which in turn leads to an adiabatic temperature change, ΔT_{ad} , as shown in **Fig. 2(b)**. Hence, ΔT_{ad} is also used for quantifying MCE, whereby its maximum is found near the magnetic transition temperature. The inter-relationship between the isothermal entropy change and the adiabatic temperature change via the temperature and field change of the total entropy of the system is represented in **Fig. 2(c)**. Further details can be found in recent review papers or textbooks (Franco *et al.*, 2018; Tishin and Spichkin, 2016).

Without going into details, the type of phase transition has a large influence on the magnetocaloric characteristics of the material. For second order phase transitions, the maximum response is relatively small when compared to top-performer materials undergoing first order phase transitions though its effect occurs in a broader temperature span. For magnetocaloric materials undergoing first order phase transitions, they exhibit sharp and narrow magnetocaloric responses, and frequently accompanied by thermal hysteresis. The ideal material would be one with a large MCE peak with a broad response and without hysteresis, however this golden combination is not easy to find in single phase magnetocaloric materials.

To overcome the limited temperature span (T_{span}) over which a relevant magnetocaloric response takes place, magnetocaloric composites have been proposed by arranging layers of different magnetocaloric materials according to their T_C . Besides this, magnetocaloric composites are developed for other motivations, which will all be further described in the following sections.

Magnetocaloric Composites

Usually, magnetocaloric materials are categorized according to the order of phase transitions they undergo, which are the first order and second order phase transitions. We can also classify magnetocaloric materials as single-phase or multiphase types. In this

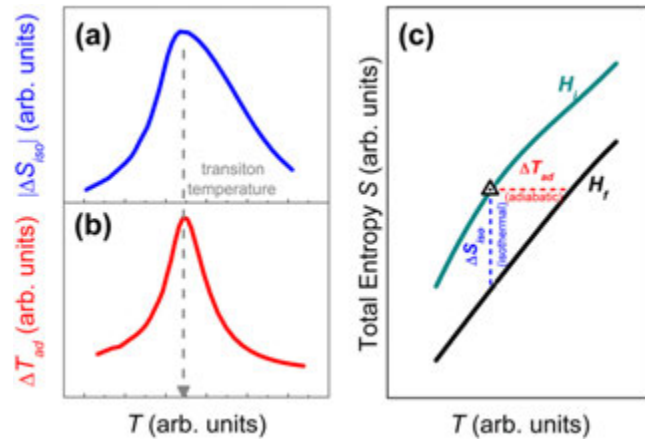


Fig. 2 The temperature dependence of (a) ΔS_{iso} and (b) ΔT_{ad} shows a maximum at the magnetic phase transition temperature. (c) The total entropy shown as a function of temperature in initial zero (H_i) and final (H_f) magnetic fields near transition temperature shows that MCE can be quantified by either ΔS_{iso} or ΔT_{ad} .

way, it is important to note that a pure phase magnetocaloric material that undergoes a second order phase transition remains as a single phase material during the transformation (as these are continuous phase transitions for which there is no phase coexistence). However, first order phase transition materials will be composed of coexisting phases in the temperature and field range where the transition takes place. As this is a characteristic of the phase transition and occurs only in a limited temperature and field range, we will not consider these as multiphase materials.

Hence, we can classify magnetocaloric composites as: (1) multiphase refrigerator beds, in which several magnetocaloric materials are combined into a single device to optimize properties; (2) multiphase magnetocaloric materials, in which several phases are combined in the same alloy either intentionally or due to the existence of impurities; and (3) multifunctional magnetocaloric composites, in which the different phases provide different functionalities, such as mechanical stability, thermal conductivity etc.

Multiphase Refrigerator Beds

The design idea of developing multilayered magnetocaloric composites originates from the motivation of overcoming the constraints of the narrow T_{span} of the MCE peak of a magnetocaloric material, whereby its working temperature range remains limited near the transition temperature (see Fig. 2(a) and (b)). Most of the magnetic refrigeration systems employ the active magnetic regenerative thermodynamic cycle for large performance and require good MCE over a wide T_{span} , which can be achieved by combining different phases into the regenerator bed in such a way that each of them has the optimal magnetocaloric response at the local temperature of each part of the regenerator (Fig. 3). Hence, it is crucial to appropriately order the different layers according to the transition temperatures of their MCE. Strictly speaking, these layered beds cannot be considered a composite material as the different phases are separated inside the bed.

A different approach to these sorted layers of materials consists in combining different phases in the refrigerator bed to form a composite. The motivation is that the Ericsson magnetic cycle, which can allow larger effective refrigeration by changing the adiabatic stages to isomagnetic field processes (Hashimoto *et al.*, 1981), requires a constant ΔS_{iso} over the appropriate operating temperature range. These design criteria cannot be fulfilled by a single magnetocaloric material for an efficient refrigeration process in either of these cycles. Back in 1977, Brown first raised that by the employment of a mixture of materials with different transition temperatures could aid the improvement of the temperature-entropy diagram and thus the refrigeration efficiency (Brown, 1977). Hashimoto *et al.* (1978a,b) then experimentally validated that the layered structural sintered material of several different compositions (and their transition temperatures) was a prospective way for the Ericsson magnetic cycle. With a composite system of $ErAl_{2.5}$, $HoAl_{2.5}$ and $Ho_{0.5}Dy_{0.5}Al_{2.5}$ with optimized mass ratios, a temperature range between 10 and 40K was covered (Hashimoto *et al.*, 1987b).

The attempt to increase the width of the isothermal entropy change peak was usually quantified by the refrigerant capacity (RC) or any of its approximations (Provenzano *et al.*, 2004), being the simplest one the product of the maximum isothermal entropy change times the full width at half maximum of the peak, also known as relative cooling power (RCP) (Gschneidner and Pecharsky, 2000). From the practical point of view, this had the limitation that very shallow and broad peaks could produce artificially large values of refrigerant capacity that cannot be used in real devices. In addition to a large refrigerant capacity, a practical material should exhibit an adiabatic temperature change in the order of 1K or above to be usable.

A schematic diagram of a biphasic A-B magnetocaloric composite showing the expansion of the temperature span of the composite is presented in Fig. 4, where it comprises of a mass fraction of 60% for the higher T_C phase (denoted as phase B) and a ΔT_C selection of 70K.

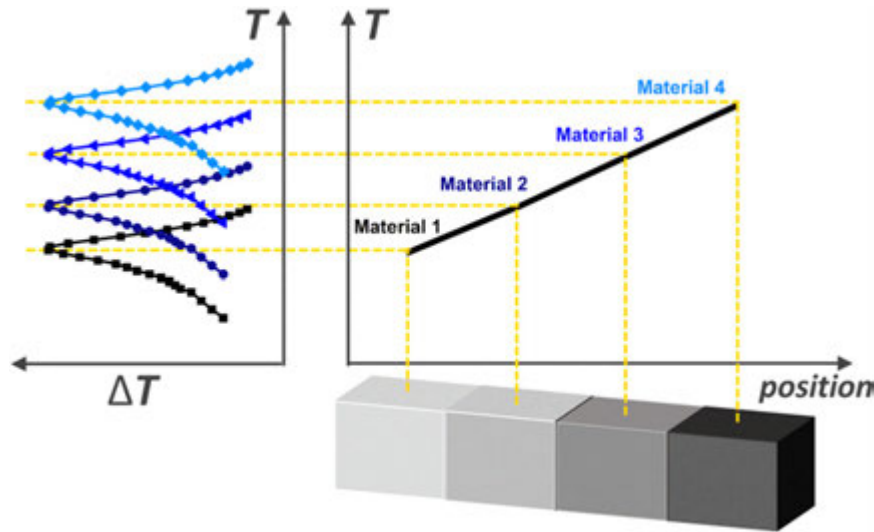


Fig. 3 Multilayer refrigerator bed in which each layer, formed by a different material, has a peak response close to the local temperature of that part of the regenerator.

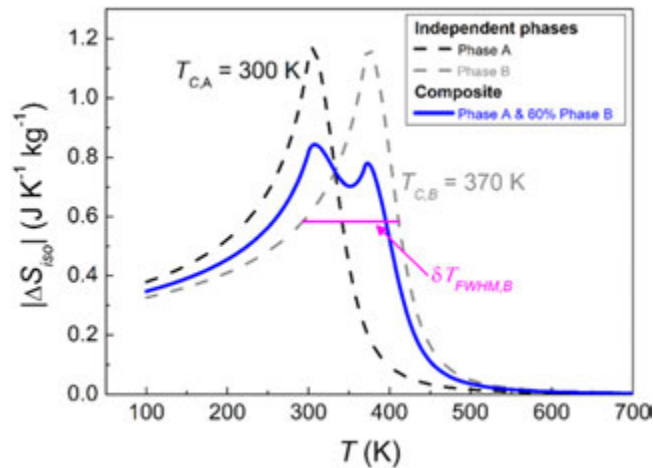


Fig. 4 A broadened effective curve (blue) of the multiphase magnetocaloric composite with phases A and B exhibiting $\Delta T_C = 70\text{K}$. The optimum phase ratio is also crucial where a mass fraction of 60% of the higher T_C phase (Phase B in this example) is selected in this case. An expansion of the temperature span is observed when compared to that of a single phase (represented by the pink line for Phase B).

Simulations of an active magnetic regenerator cycle using different materials (Niknia *et al.*, 2017) showed an excellent correlation between RCP and the maximum exergetic cooling power (especially when experimental data of real materials were used in the model; the inclusion of “synthetic”-simulated-materials provided a better correlation). This correlation between RCP and the ultimate performance of the simulated device hints at the validity of this figure of merit, provided that a required minimum adiabatic temperature change is available.

In order to avoid the artificially large RCP that can be obtained for remarkably shallow peaks, which would be unusable in experimental devices, alternative figures of merit have been defined, such as the temperature averaged entropy change (TEC) (Griffith *et al.*, 2018). This consists in the maximum average of the isothermal entropy change over a temperature interval T_{lifu} typically of 10K. The center of this interval that maximizes the average is located near the temperature of the peak entropy change but does not coincide with it due to the asymmetry of the temperature dependence of the entropy change curve.

A systematic study of layered magnetocaloric composites of $\text{Fe}_{88-2y}\text{Co}_y\text{Ni}_y\text{Zr}_7\text{B}_4\text{Cu}_1$ amorphous alloys with varying phase fractions ($y=8.25$ and 11 for Phase 1 and 2) showed the largest performance improvement of RC for a composite consisting of 64.6% mass fraction of the phase with the higher T_C (Patricopoulos *et al.*, 2012). This confirmed the predictions of a sizeable increase of refrigerant capacity when the distance between transition temperatures and the fraction of these phases is properly optimized (Caballero-Flores *et al.*, 2011). Another stacked multi-layered magnetocaloric components of metamagnetic Cu-doped Ni–Mn–In were developed with the aim to expand the T_{span} (Camarillo *et al.*, 2016). They developed a composite specimen with a total mass of 262 mg for calorimetric measurements to obtain the direct MCE response of the multi-layered system.

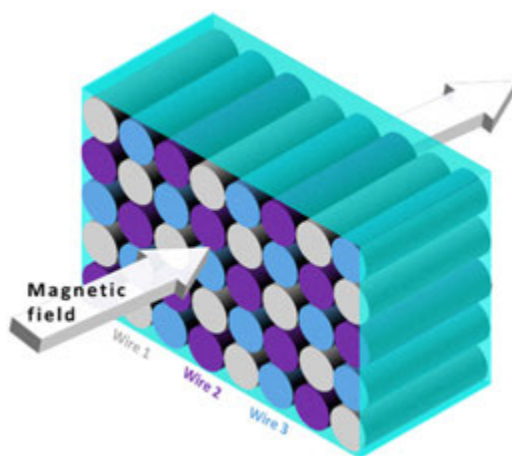


Fig. 5 Schematic illustration of the three-component magnetocaloric composite configuration of closely packed microwires of dissimilar compositions as the regenerator bed.

In addition to these studies of the magnetocaloric response of the multi-layered composite materials, Richard *et al.* (2004) experimentally verified the magnetocaloric composite of Gd and $\text{Gd}_{0.74}\text{Tb}_{0.26}$ employed as a layered active magnetic regenerators, obtaining larger temperature span than that of a single Gd layer configuration for loads up to 3.5 W.

Other than multi-layered magnetocaloric composite system, there is another configuration wherein microwires of dissimilar magnetocaloric compositions are arranged as a composite regenerator bed. Shen *et al.* (2016) reported such system based on $\text{Gd}_{50}\text{Al}_{30}\text{Co}_{20}$ – $\text{Gd}_{60}\text{Al}_{20}\text{Co}_{20}$ microwires ($\Delta T_C \sim 23\text{K}$ and mass fraction = 50%), which showed a broader $\Delta S_{\text{iso}}(T)$ curve and temperature span, resulting in a table-like MCE behavior (i.e., constant ΔS_{iso} values for an extended T_{span}), thus the overall MCE performance was enhanced as compared to the single composition. Another microwire composite system comprising of a bi-constituent melt extracted $\text{Gd}_{50}\text{Al}_{30}\text{Co}_{20}$ – $\text{Gd}_{55}\text{Al}_{20}\text{Co}_{25}$ microwires ($\Delta T_C \sim 24\text{K}$) was reported with table-like MCE behavior and enhanced performance (Bao *et al.*, 2018). Further investigation of the $\text{Gd}_{50+5x}\text{Al}_{30-5x}\text{Co}_{20}$ microwire composite system by comparing the MCE behavior of two- versus three-component composite system (Fig. 5) showed that the temperature span broadened with the number of components (i.e., the span of the T_C interval) and thus increased the overall RCP of the composite (Belliveau, 2016).

In addition, there are other composite systems which were fabricated by combining various compositions that were compacted into a bulk pellet. The selection of the alloy compositions was usually based on their MCE and transition temperatures for the optimum operating temperature range of the composite system as well as its performance (Carvalho *et al.*, 2005; Ezaami *et al.*, 2017a,b; Gębara and Pawlik, 2017). A composite of $\text{MnAs}_{0.98}\text{P}_{0.02}$ and $\text{MnAs}_{0.97}\text{P}_{0.03}$ was developed by fixing each of the phases in a polymer matrix (<8 vol.%) with the aim to optimize properties, increase T_{span} and reduce hysteresis through the composite design (Govor *et al.*, 2019).

It is worth mentioning that the strategy of improving the characteristics of a material by developing composites is radically different depending on the figure of merit that is used to evaluate the material. While RC can be largely enhanced by suitably combining chosen phases with different transition temperatures, TEC does not allow this strategy. In the case of RC, combining magnetic entropy change peaks with the same characteristics that are only shifted in transition temperature can lead to an improvement in RC with respect to the pure phases if the proper transition temperatures and fraction of phases are chosen (Paticopoulos *et al.*, 2012). However, as TEC is defined as a temperature average, the same approach cannot be followed. The TEC of a pure phase can be improved with the addition of an extra phase with a larger MCE peak if its peak temperature lays in the range of T_{if} . Therefore, in those cases that the device performance is determined by the RC magnitude (Niknia *et al.*, 2017), composites will certainly offer an improvement. If the device performance is more dependent on TEC, composites could be used to improve the performance of a low cost material by the addition of a higher peak phase (and presumably higher cost), although, most likely, the use of the high cost phase alone could be preferable. Simulations on this topic are currently being performed. Nevertheless, cost is one critical bottleneck of the road of magnetic refrigerators towards consumer market (Rowe, 2011), hence cost reduction due to the utilization of composites is an interesting area to explore.

Multiphase Magnetocaloric Materials

There is another type of magnetocaloric composites in which various phases coexisting in a single alloy or compound can affect the overall MCE behavior. They could be developed through careful compositional selection based on the phase diagram or unexpectedly appear during the alloy fabrication. In the latter case, the additional phase(s), since not pre-selected for the design of the composite, can either improve the performance with a widened T_{span} if phases have overlapping MCE, or lead to significantly smeared ΔS_{iso} values as a dilution effect.

For the case of pre-selected phases for magnetocaloric composites, $\text{Gd}_{28}\text{Ni}_{24}\text{Al}_{48}$ and $\text{Gd}_{33}\text{Ni}_{13}\text{Al}_{54}$ multiphase composites were reported exhibiting three magnetic phases, which were GdNiAl_2 , GdNiAl and Ni-substituted GdAl_2 , whose ordering temperatures were closely adjacent to one another (Ma *et al.*, 2016). The authors reported that the broadened ferromagnetic phase transitions of the composites contributed to table-like MCE behavior and considerable refrigerant capacity. Another Gd-based magnetocaloric composite exhibiting table-like MCE behavior was reported for an alloy composition of $\text{Gd}_{53}\text{Co}_{19}\text{Al}_{28}$, which comprised of Gd_2Al , $\text{Gd}_2\text{Co}_2\text{Al}$ and $\text{GdCo}_{0.74}\text{Al}_{1.26}$ crystalline phases (Fu *et al.*, 2014). In addition, the combination of amorphous structure with (nano)crystalline phase(s) in Gd-based composites was reported to exhibit table-like MCE behavior, enhancing the overall performance of the composite (Fu *et al.*, 2014; Balfour *et al.*, 2015; Gorsse *et al.*, 2008). Dong *et al.* (2015) reported that the composite of GdCrO_4 and ErCrO_4 theoretically and experimentally showed a table-like MCE behavior for a mass ratio of 1:1. In addition, Vandrangi *et al.* (2015) reported that self-assembled Mn_3O_4 – $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanocomposites showed an enhanced ΔS_{iso} compared to that of pure $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films. El Maalam *et al.* (2018) reported that $(\text{La}_{0.45}\text{Nd}_{0.25})\text{Sr}_{0.3}\text{MnO}_3$ (LNSMO) – CuO composites showed an enhanced ΔS_{iso} compared to that of LNSMO by adding 5 wt% of CuO . They found that the CuO phase mainly segregated at the grain boundaries of the composite.

A recent study where the MCE behavior of melt extracted $\text{Ni}_{45.6}\text{Fe}_{3.6}\text{Mn}_{38.4}\text{Sn}_{12.4}$ microwires was significantly improved after annealing was reported by Zhang *et al.* (2017). The authors showed that the secondary nanoscale γ -phase precipitates formed upon annealing contributed to the MCE enhancement, where the composite showed both inverse and conventional MCE, similar to typical Ni-Mn-Sn-type magnetocaloric compound.

Appropriate compositional selection of Zn additions to Gd can enable the development of an equilibrium biphasic composite of GdZn phase coexisting with Gd phase. The T_C of GdZn and Gd are in close proximity ($\Delta T_C < 27\text{K}$) and close to room temperature. The earliest investigation related to the magnetocaloric studies of this system was reported by Pecharsky and Gschneidner (1999). They studied the MCE of GdZn alloy and reported on the MCE behavior of two-phase alloys calculated from the modeled heat capacity. Other relevant reports were based on the MCE of several Gd eutectic compositions, wherein GdZn –Gd composite was included but its MCE performance less focused (Shao *et al.*, 1996a; Canepa *et al.*, 2005). A systematic study of the composite system was later reported by Law *et al.* (2016) where a RC improvement up to 45% was found for the biphasic composite as compared to the response of the single phases (Gd or GdZn) without a significant change of isothermal entropy change. Another similar report of biphasic magnetocaloric composite was found for Gd_7Pd_3 phase coexisting with Gd, wherein its ΔT_C was about 40K (Gębara *et al.*, 2020). Both of these biphasic composite systems (Gd + GdZn or Gd + Gd_7Pd_3) show an enhancement in RC when they comprise of a larger phase proportion of the higher T_C phase. The consideration of interactions among the phases does not alter the main conclusions (Romero-Muñiz *et al.*, 2013).

Systematic studies of the phase proportion on the MCE of $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ – EuO composites reported the broadening of the MCE curves and found that 40%–60% composite retained larger ΔS_{iso} values than those of 70%–30% (Chaturvedi *et al.*, 2011). This is also in agreement with earlier composite examples whereby the MCE improves when the composite system is enriched in the higher T_C phase, which is EuO in this case. Likewise, numerical results reported that with the optimum ΔT_C together with at least 50% of the composite consisting of the phase of higher T_C , under the assumption of non-interacting phases (Caballero-Flores *et al.*, 2011), improvement in the overall RC could be obtained. Numerical calculations of $\text{Dy}_2\text{Cu}_2\text{Cd}$ – $\text{Tm}_2\text{Cu}_2\text{Cd}$ magnetocaloric composite found that ~ 77 wt% $\text{Dy}_2\text{Cu}_2\text{Cd}$, the higher T_C phase, was the optimum ratio where the composite exhibited a table-like MCE response in a wide temperature span of 10–70K (Zhang *et al.*, 2016).

Another family of commonly studied multiphase magnetocaloric composites is Fe-based amorphous systems with nano-crystalline phase(s). In this case, α -Fe phase typically precipitates out from the main Fe-based amorphous phase. Due to the high T_C of α -Fe (1046K (Cullity, 1972)), its presence cannot expand the T_{span} of the residual amorphous phase (whose T_C can range from 300 to 700K, depending on the alloy composition) due to the large separation of T_C of the phases and the sum rule explains a notable dilution effect (Franco *et al.*, 2006).

A classic example of ferromagnetic phase undesired for magnetocaloric composites is found in the notable $\text{La}(\text{Fe,Si})_{13}$ compounds (Shen *et al.*, 2009). During synthesis, it is challenging to maintain the composition of their starting elements due to the easy evaporation of La, which might not only lead to large amount of α -Fe impurity phase but also affects the magnetic phase transition temperature. The additional annealing stage (at high temperatures, such as 1173–1373K for several weeks) after melting can usually reduce the impurity phase to trace amounts but not to elimination. Similar to the former example, due to the large separation between the peak temperature of the desired NaZn_{13} phase (around 190K) and that of the α -Fe phase, the presence of the latter dilutes the overall MCE of the magnetocaloric composite. Chen *et al.* (2015) reported that the increasing content of excess Fe used for developing $\text{La}(\text{Fe,Si})_{13}$ compounds led to the formation of increasing amount of impurity α -Fe at the expense of lowered desired NaZn_{13} phase. The magnetization curves explicitly showed that the total transformation of the 1:13 phase was greatly reduced with the higher concentration of α -Fe in the multiphase magnetocaloric composite, thus leading to a reduced value of the maximum ΔS_{iso} reported. Likewise, Gębara and Pawlik (2017) reported that the increase of α -Fe phase due to high-energy ball milling of $\text{LaFe}_{11.8-x}\text{Co}_x\text{Si}_{1.2}$ reduced the peak of $\Delta S_{\text{iso}}(T)$ for the composite system. On a side note, Shao *et al.* (2017) reported that using extra α -Fe as a reinforcement phase during the fabrication of La-Fe-Si-H blocks and plates could enhance the mechanical integrity.

Fe_2P -based Mn–Fe–P–Si-type compounds are also an example of magnetocaloric materials formed with impurity phases during their fabrication. Amounts of impurity $(\text{Mn,Fe})_3\text{Si}$ or $(\text{Mn,Fe})_5\text{Si}_3$ phases are usually reported alongside to the desired Fe_2P phase in the X-ray diffraction results for these compounds (Nguyen, 2012; Thang *et al.*, 2017; Lai *et al.*, 2020). Nguyen (2012) reported that though the impurity phases were irrelevant for magnetic response, their presence in the multiphase Mn–Fe–P–Si-based composites could affect the optimization of the overall MCE behavior.

Multifunctional Composites

Intentional multifunctional magnetocaloric composites are also developed with the aim of improving other properties (other than MCE) of the magnetocaloric material system, such as mechanical strength or stability, thermal conductivity, corrosion resistance etc. One common example of this category involves the combination of magnetocaloric material, usually brittle, with polymer where mechanical integrity can be substantially enhanced. An early example of such composite was reported by Pryds *et al.* (2011) who proposed a magnetocaloric composite monolithic design as it could overcome the compensation in the mechanical strength of magnetocaloric regenerator plates when the wall thickness is reduced for improving the refrigerator performance. The composite system consisted of $\text{La}_{0.67}\text{Ca}_{0.26}\text{Sr}_{0.07}\text{Mn}_{1.05}\text{O}_3$ (LCSMO) and low-density polyethylene, which acted as a binder to allow sufficient plasticity as the honeycomb structure shrinks. The authors reported an approximate 40%–45% shrinkage variation of the volume contraction for all studied composite ratios where the highest volume fraction of LCSMO they had used was 58 vol%. They further compared the performance of a parallel plate regenerator versus a monolithic design via predictions and reported that the latter exhibited similar characteristics (as well as larger surface area) as the former. A recent work by Andrade *et al.* (2020) reported flexible composites of magnetocaloric $\text{Gd}_5(\text{Si,Ge})_4$ microparticles embedded in poly(methyl methacrylate) matrix developed to aid the practical use of brittle magnetocaloric intermetallic materials in devices.

Radulov *et al.* (2015b) performed a systematic investigation of optimizing the MCE and mechanical integrity of polymer-bonded $\text{La}(\text{Fe,Mn,Si})_{13}\text{H}_x$ composites through varying the particle sizes, compaction pressure, amount and type of polymer used. The hydrogenation of $\text{La}(\text{Fe,Si})_{13}$ -type of magnetocaloric material could shift the transition temperatures to desired room temperature without compensating its MCE performance but caused the material to be in powder form. The authors reported that a composite of powders (combination of 70% 160–250 μm and 30% 0–20 μm) and 5 wt% *Epoxyharz L* shows <2% remnant porosity and a ΔT_{ad} that was comparable to the MCE of the precursor. For the composite of 5 wt% *Epoxyharz L* and 160–250 μm -sized powders, its remnant porosity increased to about 10% though ΔT_{ad} increased to 4.8K. Based on their findings, the authors recommended the following optimized parameters for developing polymer-bonded $\text{La}(\text{Fe,Mn,Si})_{13}\text{H}_x$ composites: ~5 wt% of low viscosity epoxy (density $\leq 1 \text{ g cm}^{-3}$) and powder with particle size > 200 μm , and cold compaction pressure of 0.1 GPa. Mechanical stability investigation of similar polymer-bonded $\text{LaFe}_{11.38}\text{Mn}_{0.32}\text{Si}_{1.3}\text{H}_{1.6}$ composite plates showed that the bending strength improves by ~2.4 times when the remnant porosity is halved for the composite of bimodal powder mixture (70% with 160–250 μm and 30% with 30–40 μm) as compared to that made of solely 160–250 μm -sized powders (Radulov *et al.*, 2015a). However, the performance of these polymer-bonded composite systems is limited by the low thermal conductivity of the polymer and fatigue caused by the mechanical stress arising from the large magneto-volume effect in $\text{La}(\text{Fe,Si})_{13}$ -type materials, which leads to the proposal of developing metal-bonded composites. Radulov *et al.* (2017b) fabricated such configuration by hot-dip coating $\text{LaFe}_{11.4}\text{Mn}_{0.3}\text{Si}_{1.3}\text{H}_{1.6}$ in the eutectic $\text{Bi}_{32.5}\text{Sn}_{16.5}\text{In}_{51}$ alloy to develop a metal-bonded magnetocaloric composite with 5 wt% of coating. A systematic investigation of the MCE, thermal transport, mechanical and chemical behavior of similar systems was further performed in $\text{Bi}_{32.5}\text{Sn}_{16.5}\text{In}_{51}$ -bonded $\text{LaFe}_{11.38}\text{Mn}_{0.32}\text{Si}_{1.3}\text{H}_x$ composites and further compared to polymer-bonded composites as well as $\text{LaFe}_{11.38}\text{Mn}_{0.32}\text{Si}_{1.3}\text{H}_x$ systems (Radulov *et al.*, 2017a). The authors reported that fully-dense composite plates of 25 vol% metal binder and bimodal powder showed a large ΔS_{iso} and a ~5.8% increase in ΔT_{ad} as compared to that of loose bimodal powder. They also reported that the metal-bonded composite showed good mechanical integrity (flexural strength > 100 MPa) and high thermal conductivity where both of them surpass those of the original $\text{LaFe}_{11.38}\text{Mn}_{0.32}\text{Si}_{1.3}\text{H}_x$ and polymer-bonded composite systems.

Experimental tests of the MCE of thin regenerator plates of epoxy-bonded La-Fe-Co-Si magnetocaloric composites, which consisted of various particle size fractions of La-Fe-Co-Si , as well as their performance in the active magnetic regenerator device were reported by Pulko *et al.* (2015). The authors found a beneficial influence on the thermal conductivity when employing a mixture of several particle size fractions. They reported attaining a maximum temperature span of $\sim \Delta T = 10\text{K}$ under no cooling load condition for 1.15 T. They observed no significant variations to the mechanical integrity of the composite and the stability of the measured ΔT values upon cyclic application of the magnetic field (90,000 cycles).

Zhong *et al.* (2018) studied another metal-bonded $\text{La}(\text{Fe,Si})_{13}$ -type magnetocaloric composite system of $\text{La}_{0.8}\text{Ce}_{0.2}(\text{Fe}_{0.95}\text{Co}_{0.05})_{11.8}\text{Si}_{1.2}\text{-Sn}$ with mass ratio of 9:1, showing that the mechanical properties of the composite system gave a maximum compressive strength in the range of 180–200 MPa, which was similar to that of $\text{Sn}_{42}\text{Bi}_{58}$ -bonded $\text{La}_{0.8}\text{Ce}_{0.2}(\text{Fe}_{0.95}\text{Co}_{0.05})_{11.8}\text{Si}_{1.2}$ bulk composites with fine particles (<45 μm) (Dong *et al.*, 2018). The optimum mechanical properties and MCE of the bimodal size-distributed $\text{La}_{0.8}\text{Ce}_{0.2}(\text{Fe}_{0.95}\text{Co}_{0.05})_{11.8}\text{Si}_{1.2}$ powder in the hot-pressed $\text{La}(\text{Fe,Si})_{13}$ -type-Sn composite was found for a bimodal mixture of 80 wt% coarse particles (180–250 μm) and 20 wt% of fine particles <45 μm where the density of the composite improved from 6.82 to 6.94 g cm^{-3} (Zhong *et al.*, 2019).

Other low-melting point metal binders added to $\text{La}(\text{Fe,Si})_{13}$ -type magnetocaloric composite system include $\text{La}_{0.77}\text{Al}_{0.23}$ (Fan *et al.*, 2018) and, more recently, $\text{Ce}_{40}\text{Co}_{60}$ (Zhong *et al.*, 2020). For the former, authors reported that $\text{La}_{0.77}\text{Al}_{0.23}$ could favor peritectic reaction, enabling a high content of 1:13 phase to be obtained. $\text{Ce}_{40}\text{Co}_{60}$, on the other hand, was selected to develop $\text{LaFe}_{11.6}\text{Si}_{1.4}/\text{Ce}_{40}\text{Co}_{60}$ bulk composites by combining low-temperature hot pressing sintering and high-temperature grain boundary diffusion where authors reported a table-like MCE with high RC and compressive strength.

Another system developed with the aim of addressing the limited mechanical stability of $\text{La}(\text{Fe,Si})_{13}$ -type compounds used the powder-in-tube technology to fabricate composite wires of a brittle magnetocaloric core packed in a ductile jacket (Funk *et al.*, 2018). The system comprised of core $\text{La}(\text{Fe, Si, Co})_{13}$ -based powder (within 0.58 μm tube) and austenitic seamless AISI 316 L steel tube, which could compensate the mechanical stresses of the core arising from the magneto-volume effect during the thermomagnetic

phase transition. The authors pointed out that the composite wires could also offer different possible arrangements of the wires in the regenerator other than being applicable to materials with processing difficulties. Recently, ErAl_2/Cu composite wires were fabricated to compensate for the poor malleability and ductility of lanthanide (R) Laves phase RT_2 (where $T = \text{Ni, Co and Al}$) (Yamamoto *et al.*, 2020). The authors qualitatively reported similar MCE characteristics, though reduced, as those of the powder sample and attribute that the ErAl_2 core could have undergone induced uniaxial magnetic anisotropy, which caused the decrease in MCE near the magnetic phase transition. They further indicated that additional processes, such as annealing, were recommended to increase the volume fraction of the magnetocaloric core.

Nanocomposite ribbons were developed with the aim of rectifying the fabrication challenges due to the intrinsic poor mechanical properties of intermetallic materials. Gd-based powder compositions of $\text{Gd}_{0.85}\text{Tb}_{0.15}$, $\text{Gd}_{0.75}\text{Zn}_{0.25}$ and $\text{Gd}_{0.85}\text{Y}_{0.15}$ were loaded and compacted into annealed Cu tubes that were sealed at one end (Shao *et al.*, 1996a). Upon the final sealing of the other end of the powder loaded tube, it was rolled into nanocomposite ribbons of magnetocaloric powders sheathed with Cu. The authors reported that the as-prepared nanocomposites exhibited larger specific heat and lower T_C where the nanocomposite Gd-Y showed an enhanced MCE as compared to its bulk counterpart (Shao *et al.*, 1996b).

Composites are developed for multiple purposes such as corrosion resistance, synthesis facilitation, specific applications, inclusion of other effects for performance enhancement etc. For improving corrosion resistance, additional Cu or FeNi plating as well as phenolic resin as a binder to $\text{La}(\text{Fe,Si})_{13}$ -type of materials or composites were reported (Tian *et al.*, 2013; Zhao *et al.*, 2019a; Zhang *et al.*, 2018). The addition of Ta to $\text{La}(\text{Fe,Si})_{13}$ -type materials to fabricate $\text{LaFe}_{1.2}\text{Si}_{1.8}/\text{Ta}$ composites was reported to show enhanced thermal conductivity with increasing Ta content (Wu *et al.*, 2019). Hot pressed La-Fe-Si-H/Sn composites were reported with enhanced thermal conductivity combined with good MCE (Ouyang *et al.*, 2019). Authors also included a modified Hasselman-Johnson model to predict for the thermal conductivity by considering appropriate particle size, porosity and interfacial contact conditions. For facilitating synthesis, Gavrilova *et al.* (2018) developed $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{-NaF}$ composites and reported that the presence of NaF could reduce the synthesis temperature, producing granular structure and eliminating any undesired impurities. Hybrid nanostructure composites consisting of fine Gd_2O_3 nanoparticles embedded in the pores of periodically ordered mesoporous silica with hexagonal or cubic symmetry were reported to show reasonable high MCE (ΔS_{iso} varies from 29 to 64 $\text{J kg}^{-1} \text{K}^{-1}$ for 5 T) (Zelenakova *et al.*, 2018). Their diamagnetic silica matrices served as nanoreactors for the nanoparticles growth and their symmetries affected the magnetic properties of the global composites. Hu *et al.* developed a FeRhPd/PMN-PT composite to achieve a broadened T_{span} through strain-mediated magnetoelectric coupling by applying an electric field of 8 kV cm^{-1} , which extended the T_{span} from 35 to 47 K (Hu *et al.*, 2017). The combined application of electric and magnetic fields in FeRh/PMN-PT heterojunctions allows for alternative refrigeration cycles (Qiao *et al.*, 2020). For $(011)0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$ composites, the non-volatile strain states were obtained by the application of asymmetric bipolar electric fields, leading to an increase in the phase transition temperatures and thus improved effective magnetic refrigeration temperature region (Zhao *et al.*, 2019b). Cleveland and Liang (2012) developed a composite made of $\text{Gd}_5\text{Si}_2\text{Ge}$ magnetocaloric compound and PVDF (poly(vinylidene fluoride)) piezoelectric polymer intended for energy harvesting. They reported that the phase transformation of $\text{Gd}_5\text{Si}_2\text{Ge}$ could induce a power as high as 34.5 W m^{-2} , where they claimed that this value was around 1700 times higher than that obtained by PVDF alone (0.02 W m^{-2}).

Additive manufacturing, an emerging trend of producing complex structures and designs, has been raised as a potential area of exploration for magnetocaloric materials with the consideration of improving their mechanical properties, layering and adequate process control (Kitanovski, 2020). Some of these methods, such as selective laser melting, direct laser deposition, binder jet printing, had been applied to fabricating magnetocaloric materials but post-processing is required to recover the functionality of their phases. This is further accompanied by additional problems due to the presence of undesirable impurity phases during the additive manufacturing (Moore *et al.*, 2013; Stevens *et al.*, 2018, 2019; Mostafaei *et al.*, 2018; Miao *et al.*, 2020). Alternatives would include fused filament fabrication (also known as fused deposition modeling) or inkjet printing (Al-Milaji *et al.*, 2020) although the latter is usually restricted to thinner samples. For fused filament fabrication, the currently available functional filaments in the market is just only one type, which comprises of polymer-Fe composite filaments. On the other hand, customized compositions are not straightforward to prepare as homogeneity of the particle distribution in the composites affects the overall functional properties of the composites. Díaz-García *et al.* (2020a) recently reported a customized way of producing uniform functional composite filaments with good homogeneity as well as printability with fine level of dimensional control.

Analysis Methods Related to Studying Magnetocaloric Composites and Their MCE

Most of the methods for predicting or analyzing the magnetocaloric response of composites are based on a rule-of-mixtures of magnetization of constituent phases A and B under the assumption of non-interacting phases, $M(T, H, x) = (1-x) M_A(T, H) + x M_B(T, H)$ where x represents the fraction of the phase. This makes ΔS_{iso} also additive and it has been successfully applied to obtain the respective phase fractions of magnetocaloric composites from the combination of experimental $\Delta S_{\text{iso}}(T)$ data (Law *et al.*, 2016).

Scaling laws have been widely used for studying single phase magnetocaloric materials undergoing second order phase transitions, where their ΔS_{iso} collapse onto a single universal curve (Franco and Conde, 2010). Their analysis can also reveal the presence of additional thermomagnetic phase transitions (Franco *et al.*, 2007) telling that it is a multiphase composite, despite mostly a single MCE peak is observed in some materials. The resultant scaling curves show distortions from universality in

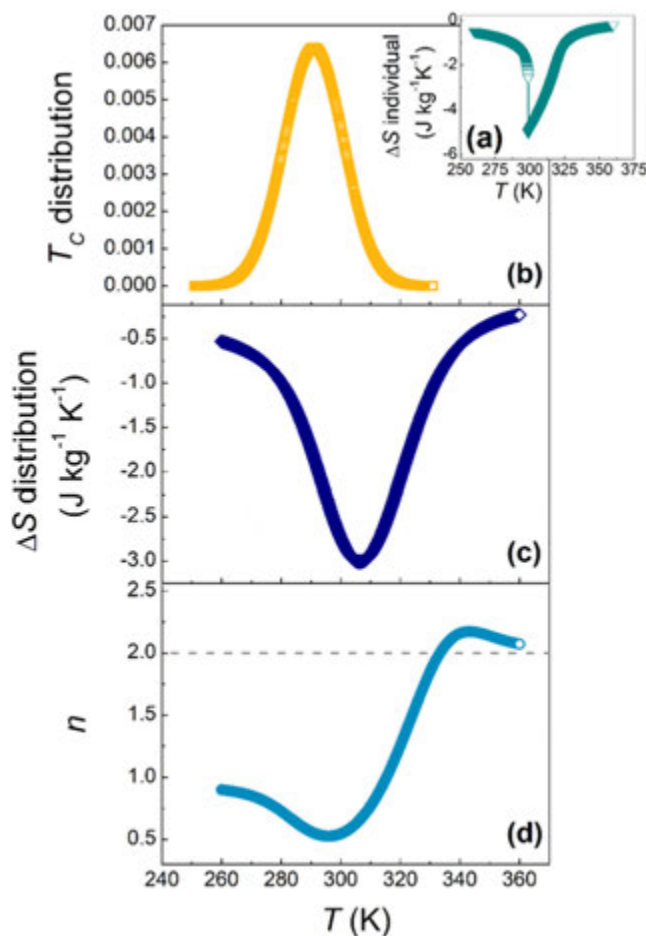


Fig. 6 Simulated composite magnetocaloric material formed by Bean-Rodbell phases with $\eta = 1.5$ (one individual phase shown in (a)) with a normal distribution of transition temperatures (composed of 500 phases) (b). Although the ΔS_{iso} of the distribution is rather smooth (c), the exponent controlling the field dependence of ΔS_{iso} shows an overshoot above 2 indicating the first order nature of the material (d).

multiphase composites (Franco *et al.*, 2009), which can get more evident when the phase fractions or MCE responses of the various coexisting phases are similar. Recently, a phase deconvolution procedure based on universal scaling of the MCE has been successfully applied to a biphasic composite for predicting the response of the pure constituent phases (Díaz-García *et al.*, 2020b). This can be useful for predicting the behavior of a pure material that could not be synthesized without additional residual contribution and to gauge the suitability of dedicating extra efforts in getting or fabricating the desired phase.

The quantification of the influence of inter-phase interactions on the performance of the material has also been a field of study over the previous years. It is notable that, depending on the technique used for identifying the strength of the interactions, values can be rather dissimilar. For example, when studying layered composites made of amorphous alloys, the interaction field obtained by analyzing RC (Romero-Muñoz *et al.*, 2013) is significantly larger than the one from FORC (first order reversal curves) analysis of hysteresis loops (Franco *et al.*, 2015). This is because the magnetocaloric response is magnified by intense magnetic fields, thus more sensitive to larger interactions, while FORC is only sensitive to fields for which the material is hysteretic and these alloys are magnetically very soft.

A particularly important point is the determination of the order of the phase transition of composite magnetocaloric materials. It is usual that authors rely on the qualitative abruptness of $\Delta S_{iso}(T)$ for this purpose, which can give erroneous results even in the case of single phase materials. More sophisticated methods, such as Kouvel–Fisher analysis for determining the critical exponents is of limited help in cases of composites where convoluted procedures have to be followed to extract reliable information (Sánchez-Pérez *et al.*, 2016). As an example of the limitation of using the shape of $\Delta S_{iso}(T)$ for this purpose, Fig. 6 shows the simulated isothermal entropy change of a composite formed by a distribution of phases following the Bean-Rodbell model with a normal distribution of transition temperatures (Fig. 6(b)). Each of the constituent phases shows a clear identifiable first order behavior (Fig. 6(a)), with a discontinuity in ΔS_{iso} , while the composite (Fig. 6(c)) shows a much smoother peak that can be wrongly identified as undergoing a second order phase transition. The use of the recently proposed method based on the field dependence of ΔS_{iso} (Law *et al.*, 2018) allows the identification of an overshoot above 2 of the exponent controlling this field

dependence (Fig. 6(d)) near the transition temperature, to unequivocally indicate that the composite undergoes a first order phase transition.

Outlook

Composite development in magnetocaloric materials has multiple aspects that spur their development. Initially proposed as a method to enhance the magnetocaloric response of materials, they evolve into multi-purpose composites today in which one of the phases provides the magnetocaloric response while the other enhances the applicability of the refrigerator bed constructed with it. The latter can be either via improvement of the mechanical integrity, added corrosion resistance, facilitation of alternative refrigerator design or by adding complementary functionality that enables the actuation over the magnetocaloric response through an alternative driving force or a modulation of the action of the magnetic field.

The optimization of magnetocaloric properties via composite design can be controversial because some of the used metrics can be artificially large for materials with little applicability. This prompts for not only development of more realistic figures of merit of the materials but also thorough tests of the developed composites in the real devices (mostly refrigerators) that will utilize them. Hence, the coexisting phases of a magnetocaloric composite should be carefully selected based on their magnetocaloric properties, magnetic phase transition temperatures as well as the optimum phase proportion ratio. The appropriate selection of these parameters is crucial for obtaining a table-like MCE (constant values in the operational temperature range) behavior, which is desirable for the Ericsson magnetic cycle as long as the overall maximum MCE is large enough (i.e., $\Delta T_{ad} > 1\text{K}$). Thus, the appropriate alloy compositions based on phase diagram can be a relevant step to develop the multiphase magnetocaloric composites with suitable ΔT_C and phase fractions.

The development of new refrigerator bed geometries deserves a separate mention. Most complicated structures cannot be efficiently produced by conventional manufacturing and there is a tendency to use additive manufacturing for this purpose. Unfortunately, most high performance magnetocaloric materials cannot withstand high temperatures without phase modification, which complicates the use of laser-based additive manufacturing methods. Polymer-based composites are the natural solution for this problem as the manufacturing process by fused filament manufacturing takes place at around the melting temperature of the polymer, which is a suitable range for the magnetocaloric fillers. The current limitations for this process are related to the filament production at the research laboratory level and the increase of the load of magnetocaloric fillers.

The opportunities in magnetocaloric composite development lie in the combination of high performing magnetocaloric phases, very well characterized in the recent years, with minority phases that will optimize applicability, manufacturability or actuation on the magnetocaloric response. It is unlikely that a radically new magnetocaloric phase will be discovered but the combination of known phases can enhance magnetocaloric properties (depending on the metric used) and that has been shown in devices and simulations. It is much more likely that multifunctional composites (i.e., combination of magnetocaloric phases with others that add extra functionality to the composite) will facilitate magnetic refrigeration to be finally implemented in mass market devices.

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Piezoelectric Polymer Composites for Sensors and Actuators

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Introduction

Currently, with the Internet of Things (IoT) and Industry 4.0 paradigms, increasingly requiring smart and multifunctional materials with higher performance, piezoelectric composites are gathering particular attention, as they can be applied in a wide range of applications from sensors and actuators to biomedical applications, being processable by conventional and additive manufacturing techniques (Baur *et al.*, 2014).

Polymer composites result from the combination of a polymeric matrix and different fillers (one or two different fillers with complementary properties), gathering the advantages of the polymeric matrix (low density and flexibility) and the fillers (mechanical and thermal properties, or increased functional response) (Akdogan *et al.*, 2005).

In relation to fillers, they can be conductive (Gong *et al.*, 2011), magnetic (Tatarenko *et al.*, 2010) and ceramic (Taunamang *et al.*, 1994), ceramic fillers having as main advantages the possibility of being piezoelectric with high piezoelectric coefficients, low dielectric and mechanical losses, and wide variety of dielectric constants (Firmino Mendes *et al.*, 2009). It is important to notice that the manufacturing method, the particle size and the dispersion method play an essential role in the final properties of piezoelectric polymer composites (Dumoulin and Deraemaeker, 2018).

In addition, piezoelectric polymer composites can be particulate (Khanbareh *et al.*, 2019) and/or laminate (Kapuria *et al.*, 2010) composites and the dispersion of each component is defined by the connectivity, that designates the interconnection of the different phases of the composite materials (Newnham *et al.*, 1978).

The connectivity influences the final structure of the piezoelectric polymer composite, which in turn influences the macroscopic response and, therefore, the application possibilities (Uchino, 2010).

One of the most recent trends in piezoelectric composites is the production of these materials with two different fillers, such as ceramic and conductive fillers (Singh *et al.*, 2017), ceramic and magnetic fillers (Ren *et al.*, 2017) and combinations thereof, such as core-shell fillers, (Chen and Liu, 2018) in order to improve performance or to provide multifunctionality for applications in areas such as dielectric-based capacitors, batteries, electronic devices and microwave absorption devices.

In the following, the main definitions and properties in relation to polymer composites will be presented, as well as recent advances divided by application. In addition, the main materials for polymers and fillers will be presented.

Piezoelectric Sensors and Actuators: Definition and Properties

The name *Piezoelectricity*, was proposed by Hankel (1881), and signifies “electricity by pressure” being derived from the Greek word *piezo* which means pressure. However, the concept of piezoelectricity was discovered a year before, in 1880, by the Curie brothers where it was found that mechanical stresses induced macroscopic polarization, i.e., the generation of electric surface charges, in several crystals such as zincblende, topaz and quartz (Curie and Curie, 1882). The converse piezoelectric effect was predicted only a year later by Lippmann, derived from the thermodynamic theory, where an external electric potential is capable of producing mechanical deformations/strains to the materials (Lippmann, 1881). With these initial discoveries, a large interest was paid in this class of materials due to their applicability in areas ranging from sonars to microphones, accelerometers and pressure transducers, among others (Tichý *et al.*, 2010).

Another breakthrough was achieved in 1969 by Kawai with the discovery of a strong piezoelectric effect in poly(vinylidene fluoride) (PVDF) adding mechanically flexible materials to the list of piezoelectric materials (Kawai, 1969). The discovery of these flexible piezoelectric materials extended the range of applications to flexible electronics, large area sensors, flexible energy harvesters and biomedicine.

By definition, piezoelectric materials, a class of dielectric materials, are a family of both inorganic and organic materials upon which polarization can be varied by the application of a mechanical stress, or vice versa, as represented in Fig. 1. They can be divided into two classes, namely polar and non-polar piezoelectric materials, depending on the existence of a net dipole moment or a null total dipole moment respectively.

In Fig. 2 it is shown a simplified molecular model explaining the behavior of a piezoelectric material. Prior to exerting an external stress to the material, in each molecule, the centers of the positive and negative charges coincide (Fig. 2(a)), i.e., the external effects of the charges are equally null, and the molecule is electrically neutral. Upon application of an external mechanical stress to the material, deformation of the internal structure of the molecule occurs and, as a result of the separation of the positive

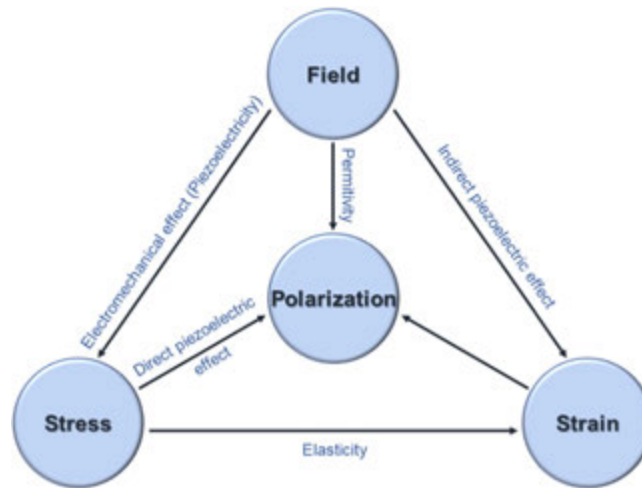


Fig. 1 Schematic representation of the sources of the piezoelectric phenomena. Adapted from Dahiya, R.S., Valle, M., 2014. Robotic Tactile Sensing: Technologies and System. Springer Publishing Company, Incorporated.

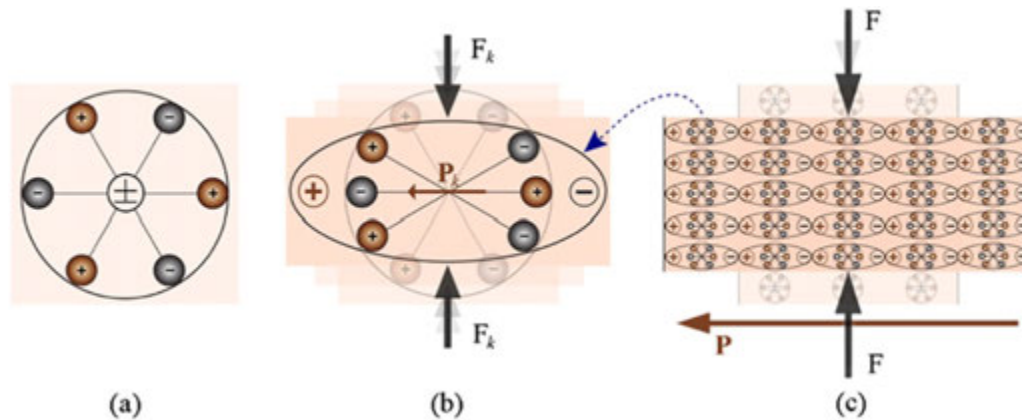


Fig. 2 Schematic representation of the piezoelectric effect: (a) electrically polarized unperturbed molecule, (b) application of an external force (F_k) and induced polarization (P_k) and (c) polarizing effect on the surface of the piezoelectric material. Adapted from Dahiya, R.S., Valle, M., 2014. Robotic Tactile Sensing: Technologies and System. Springer Publishing Company, Incorporated.

and negative gravity centers, dipoles are generated (**Fig. 2(b)**). The opposite facing poles in the material are mutually canceled and fixed charges appear on its surface (**Fig. 2(c)**) (Arnaud and Soares, 2008). This is known as the direct piezoelectric effect, schematized in **Fig. 1**. Dahiya and Valle (2014).

A year after the discovery of the piezoelectric effect, in 1881, the Curie brothers proved the theory developed by Lippmann showing that piezoelectric materials may also have the reverse behavior, i.e., when an electric potential is applied across the electrodes, a mechanical deformation/strain occurs (Lippmann, 1881). For this case it is said that the materials have a reverse piezoelectric effect (Arnaud and Soares, 2008). Materials that present this behavior can be implemented in several applications as actuators or positioning devices (Dahiya and Valle, 2014).

A schematic representation of the behavior of piezoelectric materials containing two metal electrodes deposited on the surfaces where the opposite surface charges are formed is represented in **Fig. 3**. If the electrodes are short circuited with a galvanometer connected to the wire, when pressure is applied to the piezoelectric material a charge density appears on the surfaces of the crystal in contact with the electrodes. The free charges will move until they neutralize the polarization effects as presented in **Fig. 3(a)**. Once this external force is removed, the polarization disappears with the flow of the free charges reversing and the material returning to its original state (**Fig. 3(b)**) (Arnaud and Soares, 2008). On the other hand, by replacing the short-circuiting wire with a resistance, the current would be capable of flowing through, thus converting mechanical energy into electrical energy, which is the basis of energy harvesting applications (Pinna *et al.*, 2010).

Being anisotropic by nature, piezoelectric materials mechanical, electrical and electrochemical properties vary depending on the direction of the mechanical and/or electrical stimuli and thus the implementation of such materials in the sensing and actuating areas require an in-depth evaluation of the magnitude of the various properties in the different directions (Rupitsch, 2018).

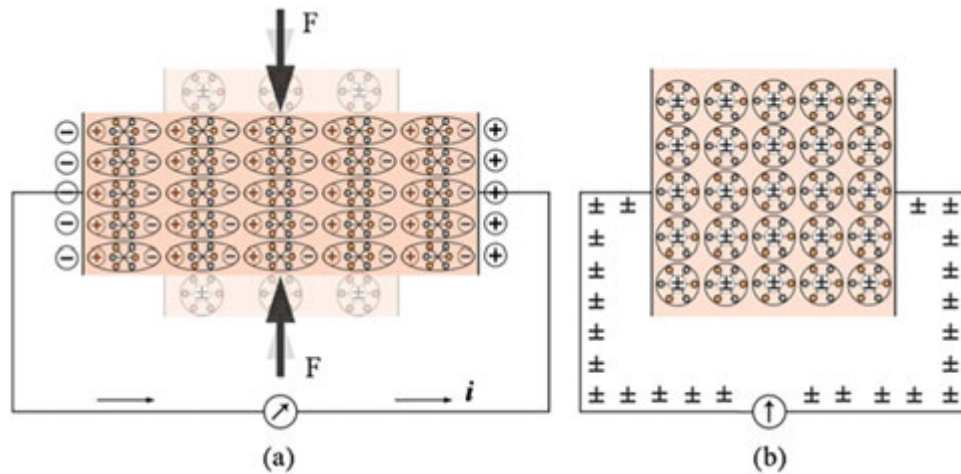


Fig. 3 Representation of the piezoelectric phenomena: (a) neutralizing current flow of a piezoelectric material with two short circuited terminal subjected to an external force and (b) material in its original state with the absence of current in the short-circuit. Adapted from Dahiya, R.S., Valle, M., 2014. Robotic Tactile Sensing: Technologies and System. Springer Publishing Company, Incorporated.

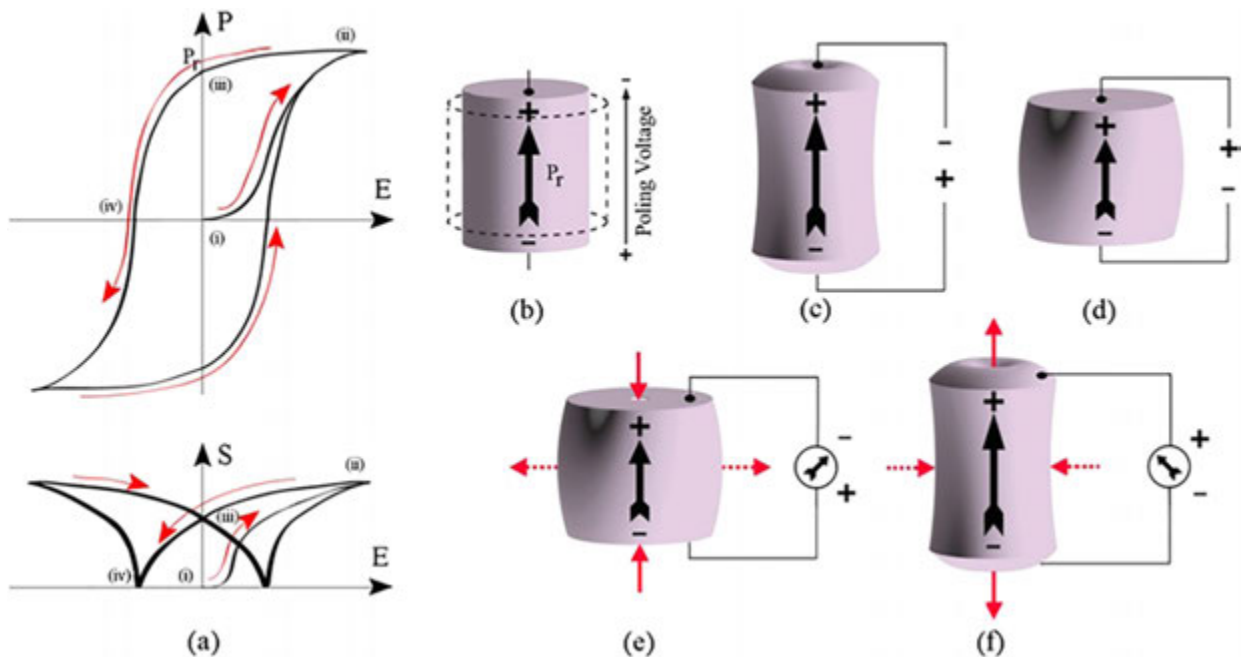


Fig. 4 Behavior of a piezoelectric material as sensor and actuator. (a) Typical P-E hysteresis and S-E plots. (b) The piezoelectric material before (dotted) and after poling, the polarity of poling field is indicated. (c) Mechanical deformation when the applied electric potential has polarity similar to the poling field and (d) when the applied electric potential has opposite polarity to the poling field. (e) Generated electric potential with polarity similar to poling field when compressive force is applied in the same direction and (f) with polarity opposite to poling field when tensile force is applied in poling direction. Adapted from Dahiya, R.S., Valle, M., 2014. Robotic Tactile Sensing: Technologies and System. Springer Publishing Company, Incorporated.

In most of the cases, the material must undergo a poling process in order to properly orient the dipoles and, thus, maximize the piezoelectric response. This poling is typically achieved by the application of an electrical field along a specific direction. Posteriorly, a smaller electric potential can be applied to the materials inducing changes in its dimensions. If this electric potential has the same direction as the poling field, additional expansion on the poling direction and contraction perpendicularly occurs (Dahiya and Valle, 2014).

In Fig. 4(a) are represented the typical polarization versus electric field (P-E) hysteresis and strain versus electric field (S-E) plots of a piezoelectric material. With the application of an electric field across a piezoelectric material, both the polarization and the strain curves, in the P-E and S-E plots respectively, follow the path (i) to (ii). Once this field is removed, a remnant polarization (P_r) and a

permanent change in the dimensions is experienced by the material, shown in the curves as the path (ii) to (iii), and a working point shift from the material occurs the plots in Fig. 4(a)). After this, two situations can occur. First, if an electric potential with the same polarity as the poling field is applied, the plots in Fig. 4(a) follow the path (iii) to (ii). Meaning that the piezoelectric material will experience expansion along the poling axis (Fig. 4(c)). On the other hand, if the applied electric potential has the opposite polarity as the poling field, the P-E and S-E plots will follow the path (iii) to (iv) and the material experiences a contraction along the poling field axis and expansion perpendicularly to it (Fig. 4(d)). For both situations, the piezoelectric material, when the electric potential is removed, returns to the poling dimensions (iii) in the plots (Dahiya and Valle, 2014).

Similarly, for the reverse piezoelectric effect, an electric potential is generated when a tensile force is applied (Fig. 4(e) and (f)). In (Fig. 4(e)) it is shown that if a compressive force is applied along or tensile force perpendicular to the poling axis, the generated electric potential will have the same polarity as the poling axis. Nevertheless, if a compressive force is applied perpendicularly or tensile force is applied parallel to the poling axis, the generated electric potential will have an opposite polarity to the poling axis (Fig. 4(f)) (Dahiya and Valle, 2014).

From a mathematical point of view, when low electric fields and/or low mechanical stress are applied, piezoelectric materials show a linear response (ANSI/IEEE, 1984). When stress is applied to a piezoelectric material, there will be a variation of the electrical polarization and, as a consequence, electric charge will be produced on the materials surface. Thus,

$$P_{pe} = d \cdot T \quad (1)$$

where P_{pe} is the piezoelectric polarization vector, d is the piezoelectric strain coefficient and T is the stress subjected to the material. Similarly, the reverse piezoelectric effect can be expressed by means of

$$S_{pe} = d \cdot E \quad (2)$$

with S_{pe} being the produced mechanical strain and E the magnitude of the applied electric field. Taking into account the piezoelectric materials elastic properties, the piezoelectric effect can be formulated as

$$P_{pe} = d \cdot T = d \cdot s \cdot T = e \cdot S \quad (3)$$

$$T_{pe} = c \cdot S_{pe} = d \cdot c \cdot E = e \cdot E \quad (4)$$

with c being the elastic constant (which relates the generated stress and applied strain as $T = c \times S$), s being the compliance coefficient (relating the produced deformation with the applied stress as $S = s \times T$) and e being the piezoelectric stress constant.

When the piezoelectric material is subjected to a strain, this has two implications. First, an electric polarization variation is generated and, for the other, an elastic stress T_e occurs. Additionally, the generated electrical polarization variation leads to an internal electric field E_{pe} variation which can be written as

$$E_{pe} = \frac{P_{pe}}{\varepsilon} = \frac{e \cdot S}{\varepsilon} \quad (5)$$

with ε being the materials dielectric constant. The application of a compressive stress in the same direction of the polarization direction will induce an electric field variation with the same polarity. Moreover, the presence of an electric field in polarization direction results in an expansion of the piezoelectric material in the same direction (Fig. 4(d)). This means that the directions of the produced and applied stresses are opposite, which is equivalent if the nature of the applied stress is tensile. This means that the produced stress T_{pe} is opposite to the piezoelectric material's deformation and, by consequence the stress generated can be written as

$$T = T_e + T_{pe} = c \cdot S + \frac{e^2}{\varepsilon} \cdot S = \left(c + \frac{e^2}{\varepsilon} \right) \cdot S = \bar{c} \cdot S \quad (6)$$

with $\bar{c}$ being the piezoelectric stiffened constant. Hence, in the presence of the piezoelectric effect the material becomes more rigid.

In a similar way, the materials dielectric response is also affected by the piezoelectric effect (Arnaú and Soares, 2008). Considering that the material, with dielectric constant ε , is placed between two electrodes and an external electric field is applied, a surface charge density σ will be generated due to the displacement of the electric charges towards the electrodes, with a magnitude $D = \varepsilon \cdot E$. In the case that the material is piezoelectric, the external electric field will also produce a strain, represented in Eq. (2). The produced strain can be positive or negative considering the direction of the external electric field with respect to the polarization direction. As mentioned before, an external electric field with the same direction of the polarization direction generates a positive strain, meaning the material expands in this direction. This expansion results in an electric potential with opposite polarity to the polarization direction, meaning that the surface charge density increases and the polarization increases as well. Consequently, by maintaining constant the electric field, the additional polarization increases the displacement of the free charges by a magnitude of $\sigma_{pe} = P_{pe}$ and the total electric displacement can be written as

$$D = \varepsilon \cdot E + P_{pe} = \varepsilon \cdot E + e \cdot d \cdot E = \bar{\varepsilon} \cdot E \quad (7)$$

with $\bar{\varepsilon}$ being the effective dielectric constant.

The piezoelectric effect is a coupling between the elastic variables, T and S , and the dielectric ones, D and E (Rupitsch, 2018). The linear tensor relations between these variables can be given as

$$S_p = s_{pq}^E T_q + d_{pk} E_k \quad (8)$$

$$D_i = d_{iq} T_q + \varepsilon_{ik}^T E_k \quad (9)$$

With s_{pq}^E being the elastic compliance tensor at a constant electric field, ϵ_{ik}^T being the dielectric constant tensor at a constant stress, d_{kp} being the piezoelectric constant tensor, S_p the mechanical strain in p direction, D_i the electric displacement in the i direction, T_q the mechanical stress in the q direction and E_k the electric field in the k direction. In the cases of semicrystalline and amorphous polymers and polymer composites (Vinogradov, 1999), the directions are commonly labelled as shown in Fig. 5.

For the specific case of PVDF, the most investigated and used piezoelectric polymer, the axis 1 corresponds to the draw or stretch direction, axis 2 corresponds to the transverse direction and axis 3 to the thickness or polarization axis (Broadhurst and Davis, 1984). Using this relation in Eqs. (8) and (9) they can be given by

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} = \begin{bmatrix} s_{11}^E & s_{12}^E & s_{13}^E & s_{14}^E & s_{15}^E & s_{16}^E \\ s_{21}^E & s_{22}^E & s_{23}^E & s_{24}^E & s_{25}^E & s_{26}^E \\ s_{31}^E & s_{32}^E & s_{33}^E & s_{34}^E & s_{35}^E & s_{36}^E \\ s_{41}^E & s_{42}^E & s_{43}^E & s_{44}^E & s_{45}^E & s_{46}^E \\ s_{51}^E & s_{52}^E & s_{53}^E & s_{54}^E & s_{55}^E & s_{56}^E \\ s_{61}^E & s_{62}^E & s_{63}^E & s_{64}^E & s_{65}^E & s_{66}^E \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \\ d_{41} & d_{42} & d_{43} \\ d_{51} & d_{52} & d_{53} \\ d_{61} & d_{62} & d_{63} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \quad (10)$$

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} \epsilon_{11}^T & \epsilon_{12}^T & \epsilon_{13}^T \\ \epsilon_{21}^T & \epsilon_{22}^T & \epsilon_{23}^T \\ \epsilon_{31}^T & \epsilon_{32}^T & \epsilon_{33}^T \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \quad (11)$$

According to Eqs. (8) and (9), there are 18 possibilities to couple the electrical and mechanical components of a piezoelectric material with each possibility belonging to one of four possible operating modes. The four main operating modes are known as longitudinal (L), longitudinal shear (S_L), transverse (T) and transverse shear (S_T), as shown in Fig. 6.

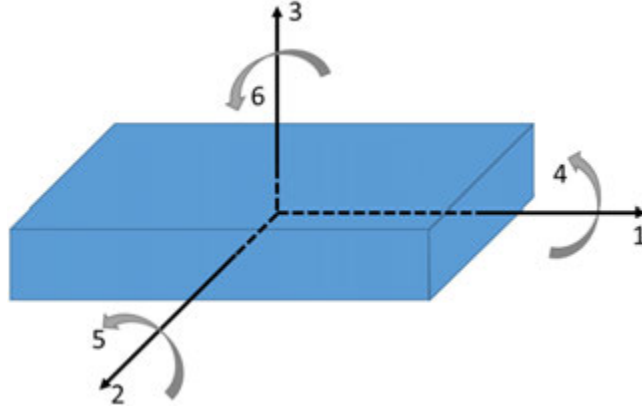


Fig. 5 Tensor directions for mechanical and elastic relations in semicrystalline and amorphous piezoelectric polymer and polymer composites.

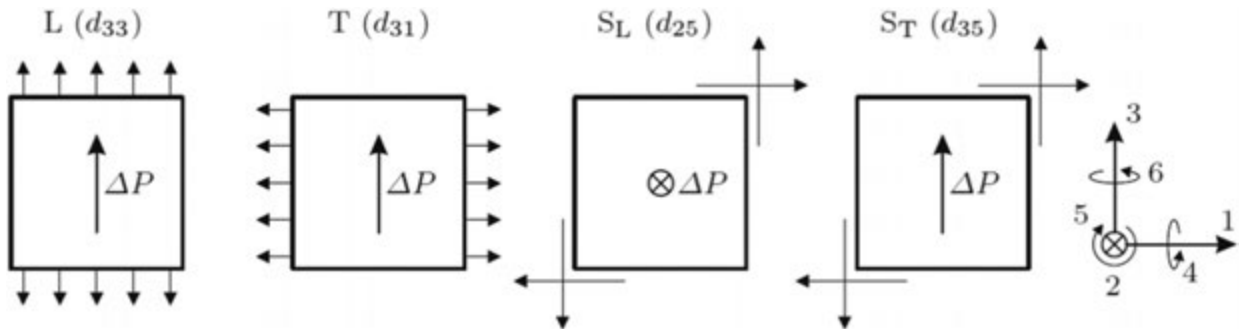


Fig. 6 Schematic representation of four operating modes of the piezoelectric effect. ΔP is the macroscopic change of the electric polarization. Adapted from Rupitsch, S.J., 2018. Piezoelectric Sensors and Actuators: Fundamentals and Applications. Berlin; Heidelberg: Springer.

As indicated before and considering the direct piezoelectric effect, a mechanical stress will lead to an electric flux density and by consequence a macroscopic change in the material's polarization in a particular direction will occur (Rupitsch, 2018). These operating modes and equivalent changes in polarization are described in Table 1.

Finally, the electromechanical coupling factor is an essential parameter, quantifying the capacity of a material to convert mechanical into electrical energy and vice-versa (Rupitsch, 2018) and can be expressed as

$$k^2 = \frac{\text{Converted electrical energy}}{\text{Input mechanical energy}} = \frac{\text{Converted mechanical energy}}{\text{Input electrical energy}} \quad (12)$$

Piezoelectric Composites: Definition and Types

Piezoelectric composites belong to the class of smart materials and typically consist of a piezoelectric ceramic filler incorporated in a piezoelectric polymer matrix. Other fillers, such as conductive and magnetic fillers, are also added to these composites, the former just for small amounts of filler as it is shown in Fig. 7. Together with those particulate composites, laminated composites, in which the materials are prepared in a layered assembly, are also often presented in the literature and implemented into applications.

Fig. 7 shows a schematic representation of a piezoelectric composite with fillers dispersed within the polymer matrix.

Polymer composite materials are characterized by low density, flexibility, excellent mechanical properties and thermal stability and higher dielectric and piezoelectric coefficient values than the pristine polymers, which result from the combination of the properties of the polymer matrix and ceramic filler (Uchino, 2010; Rupitsch, 2018).

Polymer Matrix

Several piezoelectric polymer matrices are reported in the literature, as shown in Table 2, together with the dielectric value and a relevant piezoelectric coefficient, and are divided into amorphous and semicrystalline polymers (Harrison, 2001).

In the case of semicrystalline polymers, the piezoelectricity is related with crystalline phase in which the dipolar moments can be oriented by the application of electric field (Heywang *et al.*, 2008).

Poly (vinylidene fluoride) (PVDF) is a semi-crystalline polymer that stands out in comparison to other semi-crystalline piezoelectric polymers, such as nylon-9, polyureas, poly-L-lactic acid (PLLA), poly (b-hydroxybutyrate) (PHB), among others, due to the high value of the piezoelectric coefficient ($d_{33} \sim -30$ pC/N) (Arnaú and Soares, 2008; Harrison, 2001).

Table 1 Direct piezoelectric operating modes and brief description

Operating mode	Description
Longitudinal mode, L (d_{11} , d_{22} and d_{33})	Application of a normal stress accompanied by a change in the same direction of the electric polarization
Transverse mode, T (d_{12} , d_{13} , d_{21} , d_{23} , d_{31} and d_{32})	Change in electric polarization perpendicular to the mechanical load
Longitudinal shear mode, S_L (d_{14} , d_{35} and d_{36})	Application of a shear stress accompanied by an electric polarization change perpendicular to the plane of the shearing stress.
Transverse shear mode, S_T (d_{15} , d_{16} , d_{24} , d_{26} , d_{34} and d_{35})	Change in electric polarization in the plane of the shearing stress

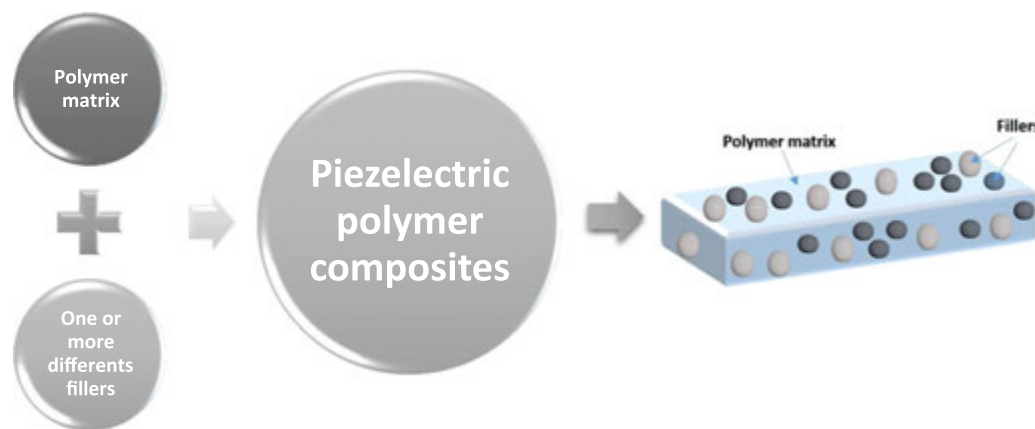


Fig. 7 Schematic representation of a particulate piezoelectric composites.

Table 2 Dielectric constant and piezoelectric coefficient for representative semicrystalline and amorphous polymers, respectively

Polymer	Dielectric constant	Piezoelectric coefficient at room temperature	References
PVDF	8–12	$d_{31} = 16$ pC/N $d_{32} = 3$ pC/N $d_{33} = -20$ to -23 pC/N	(Heywang <i>et al.</i> , 2008)
Nylon – 9	~3.5	$d_{31} = 1.1$ pC/N	(Wu <i>et al.</i> , 1986)
Polyureas	2–4	$d_{31} = 10$ pC/N	(Hattori <i>et al.</i> , 1996)
PLLA	2.8–3.5	$d_{14} = -10$ pC/N $d_{31} = 1.58$ pC/N	(Bernard <i>et al.</i> , 2017)
PHB	2–3	$d_{14} = 1.3$ pC/N	(Fukada and Ando, 1986)
Polyimide	4	$d_{33} = 0.091$ – 0.168 pC/N	(Gonzalo <i>et al.</i> , 2008)
PVDC	3.4	$d_{31} = 0.5$ – 1.3 pC/N	(Mopsik and Broadhurst, 1975)

Table 3 Dielectric constant and piezoelectric coefficient for some representative ceramic materials

Filler	Dielectric constant	Piezoelectric coefficient	References
PZT	200–5000	$d_{33} = 100$ – 1000 pC/N	(Heywang <i>et al.</i> , 2008)
BaTiO ₃	1260–1700	$d_{31} = -78$ pC/N $d_{33} = 190$ pC/N	(Gallego-Juarez, 1989)
ZnO	11	$d_{31} = -5.0$ pC/N $d_{33} = 5.9$ pC/N	(Fraga <i>et al.</i> , 2014)
KNN	250	$d_{33} \sim 63$ pC/N	(Dwivedi <i>et al.</i> , 2018)

PVDF can crystallize in at least four polymorphs known as α , β , δ and γ -phases, but the crystalline phase with best ferroelectric and piezoelectric properties is the β -phase. Commonly, β -phase films are obtained by stretching α -phase films at temperatures between 70 and 100°C and for stretch ratios from 2 until 5 and also through the addition of various fillers (magnetic: CoFe₂O₄, ceramic: BaTiO₃, ionic liquids:[EMIM][TFSI]) (Sencadas *et al.*, 2009; Branciforti *et al.*, 2007; Sencadas *et al.*, 2006; Martins *et al.*, 2014; Ribeiro *et al.*, 2018a). PVDF electroactive phase content and degree of crystallinity are influenced by the processing conditions, including stretching ratio and temperature, as well as filler type and content (Sencadas *et al.*, 2009; Sencadas *et al.*, 2006), which in turn will affect the electroactive properties of the polymer.

As in the case of amorphous polymer there are no crystalline phases, polarization results in an almost stable state due to the freezing of molecular dipoles. The amorphous polymers most reported in the literature are polyimide (Ounaies *et al.*, 1997), polyvinylidene chloride (PVDC) (Yue and Economy, 2017), poly(arylene ether nitrile) (PAEN) (Liu *et al.*, 2019), among others.

Ceramic and Other Filler Types

There are several piezoelectric ceramic materials with high piezoelectric coefficients as shown in Table 3, which also are mechanically strong, chemically inert and also show a high dielectric constant (Schneider, 2001). The most used ceramic materials in polymer composites include lead zirconate titanate (PZT), barium titanate (BaTiO₃), zinc oxide (ZnO), and lead-free as potassium niobate (KNN, K_{0.5}Na_{0.5}NbO₃), among others (Dincer, 2018).

Lead zirconate titanate (PZT) is a ceramic material with chemical formula Pb(Zr_xTi_{1-x})O₃ and perovskite crystalline structure (Cross, 1996). The phase diagram is complex, but one of the most interesting issues is the existence of the so called morphotropic phase boundary (MPB) dividing the ferroelectric region in two parts: rhombohedral crystalline phase region, rich in Zr atoms and a tetragonal crystalline phase region rich in Ti atoms. At room temperature, the MPB is placed in the region Zr/Ti = 52/48 (Amin *et al.*, 1981; Wu *et al.*, 2005). At the MPB the dielectric and piezoelectric response of the ceramic material is the largest.

Considering its high dielectric constant, BaTiO₃ is a very used ceramic material in piezoelectric polymer composites, also crystallizing in a perovskite structure (Hennings, 1987).

In addition to improved dielectric and piezoelectric properties, polymer composites with ZnO fillers show additional properties such as photocatalytic behavior (Morales-Flores and Pal, 2011).

Also, niobium-based piezoelectric ceramics are very interesting due to being lead-free, showing high dielectric and piezoelectric values, crystallizing also as perovskite structures (Kosec *et al.*, 2008).

Generally, the combination of ceramic fillers with piezoelectric polymers leads to composite materials with improved thermal and electrical properties without losing the excellent mechanical properties of the polymeric matrix.

Depending on the size of the ceramic particles, it is possible to produce micro or nanocomposites to develop piezoelectric composite materials with the desired properties for applications. Finally, the processing conditions affect their morphology, physical properties, as well as the macro and microscopic response of these materials, printing technologies allowing to produce large-area composite materials at low processing cost (Zhang *et al.*, 2016).

Other interesting composites are magnetoelectric ones (Martins and Lanceros-Méndez, 2019), which are being investigated for sensors, data memories, energy collectors, antennas or biomedical applications both as particulate or layered composites. Magnetoelectric materials result from the addition of magnetostrictive fillers, such as $\text{Zn}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$ (ZMFO) or CoFe_2O_4 (CFO), in a piezoelectric polymer matrix, such as poly(vinylidene fluoride trifluoroethylene) (P(VDF-TrFE)) (Martins *et al.*, 2015) in order to obtain magnetic and magnetoelectric response due to the coupling of the magnetostrictive and piezoelectric phases, allowing manipulation of the electrical polarization by a magnetic field or the magnetization by a field electric (Martins and Lanceros-Méndez, 2013).

Applications

Piezoelectric composites are optimized for specific applications ranging from mechanical structures to electronic devices, for areas including automotive and aerospace to structural health monitoring and biomedicine. Also, prominent applications of these materials are already found in high energy storage capacitors (Akdogan *et al.*, 2005; Qi *et al.*, 2011).

Proper selection of piezoelectric material is an essential parameter, as it directly influences the device's functionality and performance. The piezoelectric response is generally higher in piezoceramics and therefore make them the most commonly used material. However, piezoceramics are naturally brittle, limiting the strain that it can provide or absorb without being damaged. These materials are susceptible to the growth of fatigue cracks when subjected to high frequency cyclical loads. On the other hand, there are piezoelectric polymers which are flexible, acoustically well matched to water and able to be produced in large areas and in a variety of shapes. Nevertheless, the low electromechanical coupling and lower dielectric constant, limit their applications. In this way, composite appears as a way to improve properties when compared to single phase materials, being also able to produce high piezoelectric output performance (Yun *et al.*, 2014; Schmidt *et al.*, 2014).

Electronic Applications

Most periods of technological development have been distinguished by specific materials, such as stone, bronze and iron age. Currently, one of the driving forces of technology is the use of multifunctional materials, piezoelectric materials being a paradigmatic example of this demand, in particular in development of electronic devices (Akdogan *et al.*, 2005; Gupta and Srivastava, 2010).

In automotive and aerospace applications there is an increasing need for sensors and actuators. Composites based in lead zirconate titanate and PZT embedded in PVDF have been investigated as sensors in application like benders, tire pressure and knock sensor (Kulkarni *et al.*, 2018; Shirinov and Schomburg, 2008). Tire pressure sensors based on PZT-PVDF composites are directly bonded to the inner tire (Van Den Ende *et al.*, 2012).

Protection of spacecraft from radiation used in submarines, seismic and geological research are areas in which piezoelectric materials have been implemented (Rus *et al.*, 2010; Parali *et al.*, 2014; Li *et al.*, 2012; Chocat *et al.*, 2011), mainly in acoustic applications. Piezoelectric microphones based on PVDF have been developed to detect sound inside the cochlea, allowing cochlear implants with normally occurring sound pressures and frequencies (ear canal pressures > 50 – 60 dB SPL and 0.1 – 10 kHz) as shown in Fig. 8 (Park *et al.*, 2018). Piezoelectric Parylene-C (ortho-chloro-p-xylylene) polymer has been also used in microphones and actuators applications (Kim *et al.*, 2013).

Currently, with the emergence of mobiles and smart gadgets, as well as wearable electronics and soft robotics, electronic technology has directed new efforts in the development of devices and materials compatible with high touch sensibility and flexible substrates design requirements (Deutz *et al.*, 2015; van der Zwaag *et al.*, 2013; Tressler *et al.*, 1998). PVDF and reduced graphene oxide have been described as capable of producing a flexible film with microstructures to mimic the epidermal and dermal layer of human fingerprint. This sensor can identify and distinguish between multiple spatiotemporal tactile stimuli including static and dynamic pressure, temperature and vibration with high sensitivities. Thus, in artery vessels, it is possible a precision detection of acoustic sounds and the evaluation of different surface textures can be performed. Wearable devices are an important milestone not only in electronics but also in the field of biomedicine (Park *et al.*, 2015). For the evaluation of structural dynamic strains, flexible nanocomposite sensors using carbon black (CB) fillers and polyvinylidene fluoride (PVDF) matrix was fabricated, the nanocomposite allowing to detect extremely weak strains associated with sources such as structural damage, high-frequency vibration, and ultrasonic waves. This nanocomposite is adequate for strain sensor applications such as advanced bioelectronics, ultrasonic inspection, and in-situ structural health monitoring (Xu *et al.*, 2017).

A DC current sensor device based on a laminated PVDF/Metglas magnetoelectric composite was developed with the ME coefficient (α_{33}) of $34.48 \text{ V cm}^{-1} \text{ Oe}^{-1}$, a linear response ($R^2 = 0.998$) with a sensitivity of 6.7 mV A^{-1} (Castro *et al.*, 2018).

Energy Harvesting

Energy harvesting consists in the process of acquiring the surrounding energy of a system and translating it into usable electrical energy.

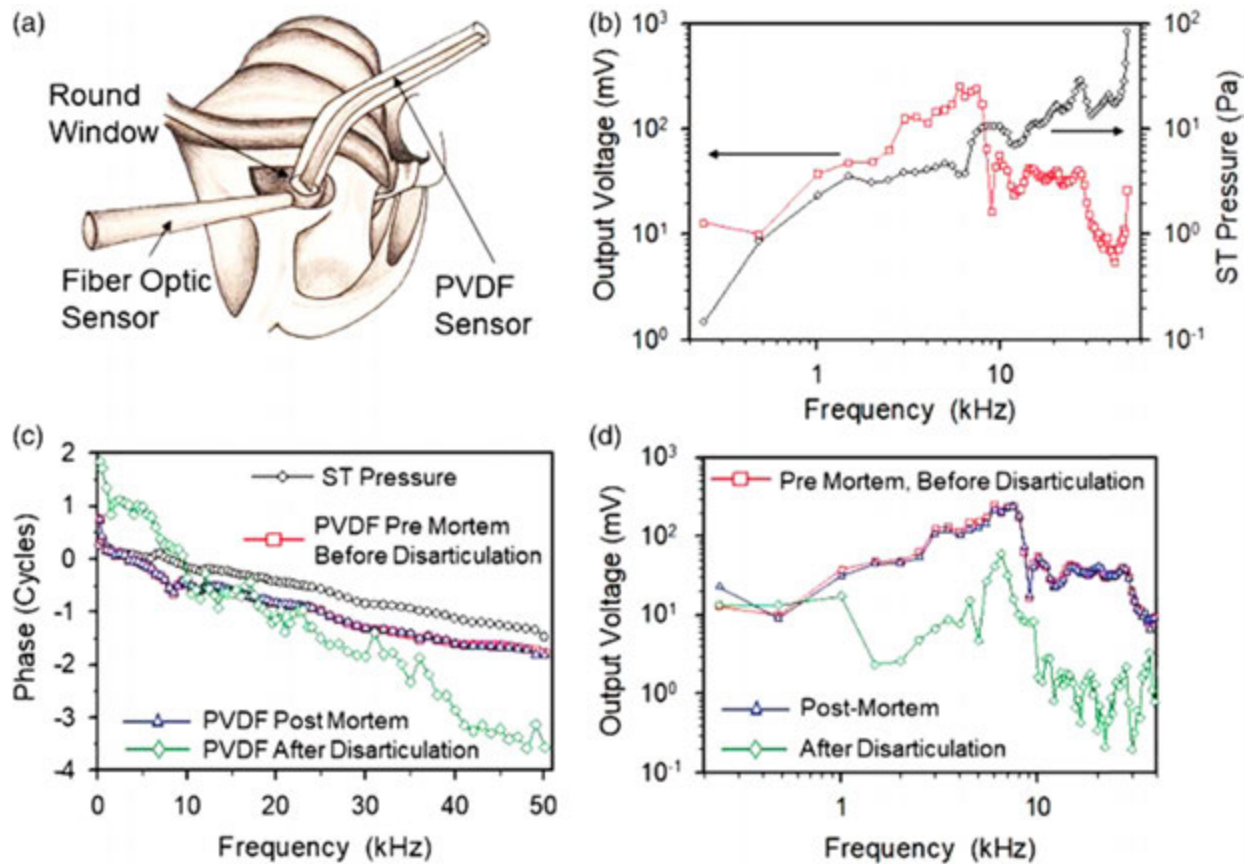


Fig. 8 (a) Schematic representation of fiber optic and PVDF pressure sensor inserted into the round window of a gerbil cochlea. (b) Plot of output voltage (after a gain of 1000) measured with PVDF sensor (red square) and pressure in the scale tympani measured with fiber optic pressure sensor (black circle). (c) Plot of phase measured with fiber optic pressure sensor (black circle), PVDF sensor premortem and before disarticulation (red squares), postmortem (blue triangles), and after disarticulation (green diamonds). (d) Plot of output voltage (after a gain of 1000) measured with PVDF sensor premortem or before disarticulation (red squares), postmortem (blue triangles), and after disarticulation (green diamonds). Adapted from Park, S., *et al.*, 2018. PVDF-Based Piezoelectric Microphone for Sound Detection Inside the Cochlea: Toward Totally Implantable Cochlear Implants. *Trends in Hearing* 22, (2331216518774450).

Piezoelectric transduction is an approach that has received attention in the area of electromechanical energy harvesting, i.e., the generation of electrical energy from mechanical vibrations (Inman, 2011; Costa *et al.*, 2019). ZnO nanowires (Wang and Song, 2006), lead zirconate titanate (PZT) nanofibers (Anton and Sodano, 2007; Chen *et al.*, 2010), barium titanate (BaTiO_3) (Anton and Sodano, 2007; Park *et al.*, 2012; Nunes-Pereira *et al.*, 2015) and PVDF (Chang *et al.*, 2010) are examples of piezoelectric materials that have been used to construct nanogenerators and to effectively power small electronic devices, such as lighting up LEDs (Pan *et al.*, 2013). In this context, FAPbBr_3 nanoparticles (cubic perovskite structure) uniformly mixed with Polydimethylsiloxane (PDMS) and then spin-coated onto an indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrate and integrated with aluminum (Al), demonstrate a high performance as energy harvesting devices. The FAPbBr_3 -PDMS composite generates electric potential under an external stress with output voltage and current density of 8.5 V and $3.8 \mu\text{A cm}^{-2}$, respectively, the nanoparticles serving as the energy generation sources as shown in Fig. 9. The generated energy can be used to charge a capacitor and light up a LED through a bridge rectifier (Ding *et al.*, 2016).

A primary motivation for self-charging structures is to use them for powering small electronic components. Piezoelectric shoes, electronic skin and other energy harvesting devices have been developed to take advantage of the produced vibration from human body activities such as: walking, running, breathing, and dancing to power-up low power electronic devices (Paulides *et al.*, 2011).

The possibility of harnessing the energy lost from a biological activity to provide energy for low-powered electronic devices has been also explored. Cardiac and lung motions serve as inexhaustible sources of energy during the lifespan. One of the first highlights in this area (Häusler and Stein, 1984) is related with the use of an implantable physiological power supply using PVDF films. The prototype, that used the energy expended for breathing, was implanted *in vivo* on a mongrel dog and demonstrated a peak voltage of 18 V, which corresponds to a power of about 17 mW. Since then, there are several proposals for such devices that translate heartbeat vibrations into electrical energy using piezoelectric composites also for directly powering a cardiac pacemaker by harvesting the kinetic energy of heartbeat (Li *et al.*, 2019). Briefly, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -(28%)- PbTiO_3 (PMN-PT) was employed as piezoelectric layer and each side was sputtered with Cr/Au. A beryllium bronze foil was used to

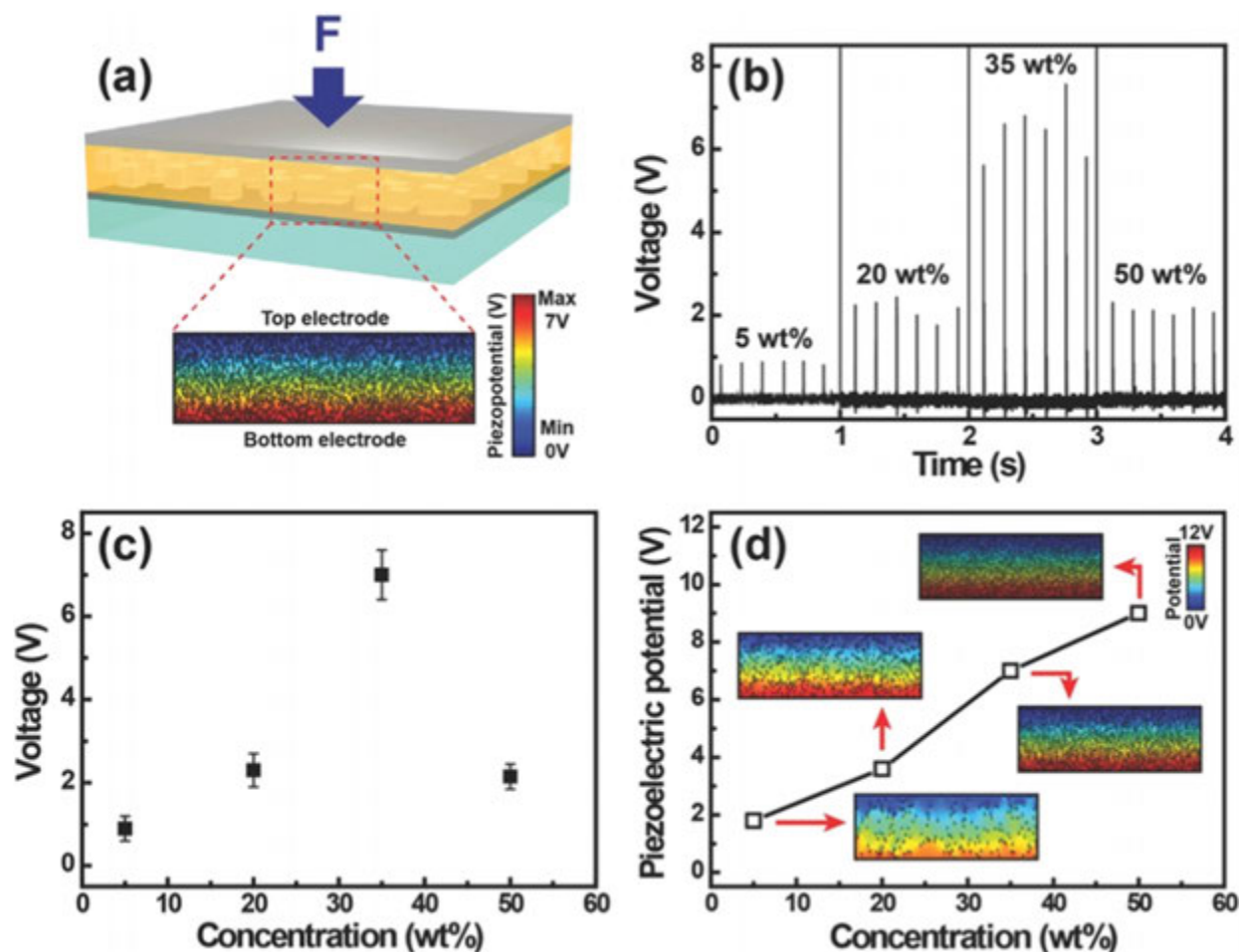


Fig. 9 (a) COMSOL simulation model of a nanogenerator. The simulated piezoelectric potential distribution inside the composite between top and bottom electrodes is indicated by color code. (b) Output voltage from nanogenerators with different FAPbBr₃ nanoparticles concentration. (c) Variation of the output voltage with different FAPbBr₃ nanoparticles concentrations. (d) COMSOL simulation result of output potential distribution of the nanogenerator with different FAPbBr₃ nanoparticles concentration. Adapted from Ding, R., *et al.*, 2016. Flexible piezoelectric nanocomposite generators based on formamidinium lead halide perovskite nanoparticles. *Advanced Functional Materials* 26 (42), 7708–7716.

provide uniform stress distribution to the piezoelectric layer and then a PDMS film was deployed by spin-coating. To further improve the stability of the device and avoid potential erosion in the *in vivo* environment, a parylene film was deposited onto the PDMS film to form a compact and hole-free coating layer. *In vivo*, a commercial cardiac pacemaker was directly powered by the implantable piezoelectric energy generator and monitored its behavior. It was concluded that patients do not need surgical replacement, or at least, the battery replacement will be less frequent. Currently, one of the most important application of energy harvesters is powering implantable biomedical devices (Yang *et al.*, 2018).

Environmental Sensors

Industrialization is causing serious problems in the environment. The accumulation of contaminants in air, soil and water is a threat that instigates the science attention. A very important environmental challenge is water remediation (Inman, 2011), knowing this, physical adsorption, biological methods and chemical oxidation have been applied worldwide (Chawla *et al.*, 2017; Li *et al.*, 2017).

Photocatalytic oxidation has been explored for environmental treatment and purification and coupled with this, piezocatalysis arises. The electric field generated by piezoelectric materials separates free electrons-holes pairs, which further react with dissolved oxygen molecules and water to decompose organic pollutants (Liu *et al.*, 2020). ZnO, MoS₂, Pb(Zr_{0.52}Ti_{0.48})O₃, NaNbO₃, and BaTiO₃ have been extensively investigated. It has been demonstrated the applicability of MoS₂/PDMS nanocomposite as piezocatalyst. The MoS₂/PDMS film was used as negative layer, while a copper thin layer acted as a positive electrode, the triboelectric nanogenerator was posteriorly fabricated for energy harvesting by hydropower. The piezoelectric part exhibited catalytically active surface on the active edge sites forming free radical oxygen to decompose pollutants. Besides the composite acting as piezocatalyst and energy harvester, it could be utilized as an active sensor for the monitoring of flowing water and its contamination (Lin *et al.*, 2017).

Table 4 Representative piezoelectric polymer composites for different application

Composite	Functional characteristic	Application	References
PVDF-TrFE/ZnO	Pressure sensing	Sensors	(Karumuthil <i>et al.</i> , 2020)
Polydopamine (PDA)-modified BaTiO ₃ /PVDF	Pressure sensing	Sensors	(Yang <i>et al.</i> , 2020)
PVDF/polyamide(PA6)/BaTiO ₃	Triboelectric nano-generator	Energy harvesting	(Sun <i>et al.</i> , 2020)
PVDF-TrFE/ single-walled carbon nanotubes (SWCNTs)	Piezoelectricity	Energy harvesting	(Shepelin <i>et al.</i> , 2020)
Sn ₃ O ₄ /PVDF	Photocatalytic	Environmental	(Han <i>et al.</i> , 2020)
Ag-TiO ₂ /PVDF-HFP	Photocatalytic and antimicrobial	Environmental	(Salazar <i>et al.</i> , 2020)
PVDF/Graphene oxide (GO)	Electrical stimulation	Biomedical	(Shuai <i>et al.</i> , 2020)
Graphene(G)/ BaTiO ₃ /PMMA	Piezoelectricity	Biomedical	(Tang <i>et al.</i> , 2020)

Atmospheric monitoring with specific sensors for organic and inorganic pollutants, potentially toxic elements, and pathogens contributes to the sustainable development of society. Traditional analytical approaches for pollutants monitoring include various chromatographic techniques. However, the response times and high mass sensitivity of a piezoelectric resonator leads to the application of chemical sensors for detecting components (ions, molecules, their fragments or clusters) (Kuchmenko and Lvova, 2019).

A different type of environmental monitoring, although an application with added value, is the use of PVDF fibers with potential to detect stress and strain in the fluid flow, including oceanic current monitoring (Egusa *et al.*, 2010).

Biomedical Applications

One of the main effort in the biomedical area is in the development of measuring equipment and health monitoring devices that seek to improve the life quality (MirHojjat *et al.*, 2015). Electronic skins or e-skin have received considerable attention in recent years for being a platform for continuous and real-time monitoring of human physiological signals. It finds potential in prosthetics, robots, wearable devices, artificial intelligence, medical equipment, and many other areas. Piezoelectric materials play a significant role in this field (Jason *et al.*, 2017; Chen *et al.*, 2018).

Owing to their properties – flexibility, biosafety, easy process –, ZnO, PVDF and BaTiO₃ are good candidates for electronic skin applications. In a study using composite nanogenerator based on PVDF fibers, it was verify that the device can be used as a sensor for real-time monitoring of radial artery pulse and respiratory information (Chen *et al.*, 2017). Also, PVDF-TiO₂ nanofibers shown its potential applications in wearable healthcare monitoring systems and the ability of self-cleaning, since TiO₂ can efficiently degrade organic pollutants (Dong *et al.*, 2017). A device for human motion monitoring was developed based on PVDF nanofibers with tetragonal-phase BaTiO₃ NWs and a wireless circuit system (Guo *et al.*, 2018). This device allows that signals from human movement are transmitted wirelessly and displayed in a mobile phone over a long distance (8 m). The results show the potential in wearable medical electronics in the fields of rehabilitation and sports medicine (Guo *et al.*, 2018).

When properly processed, piezoelectric materials represent a powerful biomaterial that, in addition to being used as bioelectronic and biomechanical monitoring devices, can interact strictly with biological tissues (Chorsi *et al.*, 2019). Tissue engineering, which is an engineering branch attempting to mimic, in vitro or in vivo, cellular microenvironments through scaffolds systems, has also taken advantage of the piezoelectric potential. Piezoelectric materials are used in the production of scaffolds since they reproduce the electrical and mechanical cues existing in the tissues. Thus, piezoelectric scaffolds act as actuators in cellular behavior to promote natural tissue formation (Ribeiro *et al.*, 2015). PVDF and its copolymers have already proven their potential in bone (Ribeiro *et al.*, 2016), skeletal muscle (Ribeiro *et al.*, 2018b) and neural (Royo-Gascon *et al.*, 2013) tissue engineering. Furthermore, it was confirmed that the incorporation of different fillers, such as cobalt ferrites (Co₂FO₄), magnetite (Fe₃O₄) or Terfenol-D, in PVDF matrix or silk fibroin matrix, ensure the natural regeneration of bones (Brito-Pereira *et al.*, 2018; Maciel *et al.*, 2018). Another study with a copolymer of PVDF, P(VDF-TrFE) revealed that the incorporation of ZnO nanoparticles promote blood vessel formation (angiogenesis) – one of the main problems in tissue engineering approaches. This study also conclude that a composite scaffold favored its integration into the surrounding tissue when compared with non-composite scaffold (Augustine *et al.*, 2017).

In summary, taking into account their versatility, piezoelectric polymer composites are used in several applications from electronics to biomedical applications, Table 4 showing representative composites in different application areas.

Conclusion

Piezoelectric polymer composite materials are a class of materials that belong to smart and multifunctional materials. The ability to transduce mechanical to electrical signals and vice-versa provide their materials with increasing technological interest for the development of sensors and actuators or energy harvesters in the form of thin, flexible and potentially large area films. This material class combines the excellent properties of ceramic fillers and polymeric matrix, allowing high dielectric constant and piezoelectric coefficient and excellent thermal and mechanical properties, being successfully implemented in areas such as consumer electronics, aerospace and automotive applications or biomedicine.

Future trends are the continuous development of multifunctional tricomposites with two different fillers, the use of environmental friendlier materials, the precise tuning of control material properties for specific applications and to improve integration into devices by techniques such as additive manufacturing techniques.

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Magnetic Shape Memory Composites

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Nomenclature

FM Ferromagnetic
MFIS Magnetic field induced strain
MMSM Metamagnetic shape memory
MNP Magnetic nanoparticles
MSM Magnetic shape memory
MSMA Magnetic shape memory alloy

MSMC Magnetic shape memory composite
MT Martensitic transformation
NP Nanoparticle
PU Polyurethane
SM Shape memory
SMP Shape memory polymer

Glossary

Magnetic field induced strain Rearrangement of martensitic variants due to an external magnetic field.

Magnetic shape memory alloys Ferromagnetic materials that exhibit the thermoelastic martensitic transformation and rearrangement of martensitic variants by applying a magnetic field, in addition to temperature and/or stress changes as in conventional shape memory alloys.

Martensitic transformation It is a diffusionless shear transformation. The transformation is commonly driven by mechanical deformation or by a change in temperature, but it can also be driven by a magnetic field.

Oligocrystalline structure Structures that have a high free surface area and few grain boundaries.

Shape memory alloys Metallic, ceramic or polymeric materials that exhibit unusual behavior when subjected to mechanical load and/or temperature change.

Introduction

Magnetic Shape Memory Alloys

Magnetic shape memory alloys (MSMAs), also known as ferromagnetic shape memory alloys (FSMAs), exhibit a diffusionless martensitic phase transformation between a high symmetry austenitic phase that is stable at high temperature and a lower symmetry martensitic phase that is stable at lower temperatures. In MSMAs, the switching among these two phases is commonly triggered by a magnetic field but it can also be driven by a change in temperature or mechanical deformation as in conventional shape memory alloys (SMAs).

Since the discovery in 1996 (Ullakko *et al.*, 1996) of large magnetic field induced strains (MFISs) in Ni_2MnGa Heusler alloys associated with magnetic-field-induced reorientation of martensitic variants, the study of MSMAs has been a topic of extensive research. In particular, Ni_2MnGa alloys undergo a structural transformation from the ferromagnetic (FM) high temperature cubic $L2_1$ phase to the tetragonally distorted 5M, 7M or nonmodulated martensitic phases.

One of the main drawbacks of the non-magnetic shape memory alloys (SMA) is their slow dynamic response restricted by thermal activation. It has been observed that the magnetic control of the shape memory leads to a much faster dynamic response when compared to thermal control (Li *et al.*, 2016). Thus, these alloys are envisaged as a promising class of smart materials to be used in actuators (where the large MFIS and magnetic shape memory effect is advantageous) and sensors (related to the dependence of the magnetization change under an external compressive stress).

Although Ni–Mn–Ga is the most widely studied system among MSMAs, there is a growing interest in developing new MSMAs, such as Fe–Pd (Steiner *et al.*, 2016; Kakeshita and Ullakko, 2002), Fe_3Pt (Kakeshita and Ullakko, 2002; Fukuda *et al.*, 2014), Ni_2MnAl (Fujita *et al.*, 2000), Ni_2FeGa (Oikawa *et al.*, 2002), or Co–Ni–Ga (Wuttig *et al.*, 2001), with enhanced properties for specific applications.

Magnetic Shape Memory Composites

The term SMA composite was first introduced by Rogers (1988) in 1988. In this pioneering work, the authors embedded Nitinol wires in a laminated polymer matrix composite to engineer hybrid intelligent composites with “multifunctionality” or adaptive properties. The goal was to take advantage of the high damping capacity, large recoverable strains and remarkable property changes due to thermal or stress-induced martensitic transformation. Since then, the interest in SMA composite materials has greatly expanded and many different types of shapes (e.g., fibers, particles, ribbons, etc.) and materials (ceramic, polymeric, metallic, etc.) have been explored for a wide range of purposes. SM composites, with either SMA acting as reinforcement or as the matrix, have emerged as promising smart systems and, hence, have been the subject of active investigations (Wei *et al.*, 1998; Lester *et al.*, 2015).

Table 1 Polymer-based composites with magnetic shape memory reinforcement

MSM reinforcement	Reinforcement type	Matrix material	MFIS	Tan δ	
Ni _{50.4} Mn _{29.9} Ga _{19.7}	Spherical particles	Silicone (Elastosil M4400)		0.14	(Feuchtwanger <i>et al.</i> , 2018)
Ni _{50.3} Mn _{28.8} Ga _{20.90}	Wires	Araldite LY 3297/ Aradur 3298 epoxy		0.1 up to 70°C, 1.7 at 115°C	(Glock <i>et al.</i> , 2014)
Ni–Mn–Ga	Particles	Lord PU		1.138	(Feuchtwanger <i>et al.</i> , 2005)
Ni _{48.3} Mn _{30.7} Ga _{21.0}	300 μ m particles	Hysol 9484		0.6	(Hannula <i>et al.</i> , 2012)
Martensitic Ni _{50.9} Mn _{27.1} Ga ₂₂	Single- and oligo- crystalline particles	Epoxy resin	0.1		(Kauffmann-Weiss <i>et al.</i> , 2012)
(Ni ₅₀ Mn ₂₈ Ga ₂₂) O _{99.97} Bi _{0.03}	Single-crystalline particles	Silicone rubber	4% and –2% (0.7 T)		(Sratong-On <i>et al.</i> , 2019)
Ni ₅₅ Mn _{20.6} Ga _{24.4}	< 74 μ m particles	Epoxy resin	0.095%		(Sun and Xie, 2010)
Ni–Mn–Ga	1 mm ² diameter single crystal rods	Epoxy resin	5%		(Glock <i>et al.</i> , 2015)
Ni _{49.9} Mn _{29.1} Ga _{21.0}	Bilayer	Dupont polyurethane	– 1%		(Gans and Carman, 2006)
Ni _{49.8} Mn _{28.5} Ga _{21.7}	Particles	Bisphenol-A epoxy resin	0.0040	0.08	(Tian <i>et al.</i> , 2014)
Ni ₄₅ Co ₅ Mn _{36.6} In _{13.4}	Particles	Epoxy resin	1.76%		(Liu <i>et al.</i> , 2010)
Ni _{51.2} Mn _{26.6} Ga _{22.2} 10M martensite	Powder	Epoxy resin		0.06	(Glock and Michaud, 2015)

In single crystals, twin boundaries can be easily moved, thus yielding the highest values of strain. In polycrystalline materials, shape changes of individual grains that appear during a twin boundary motion are not correlated, and the different grains hinder each other, thereby rendering lower strains. However, single crystals tend to be brittle and their preparation techniques are challenging and expensive. In this context, composite materials where a single crystalline/oligocrystalline reinforcement phase is incorporated in a polymeric matrix became a suitable approach to obtain materials with enhanced performance.

In particular the integration of MSMA into composite materials has emerged as a feasible approach to overcome the limitations existing in Ni–Mn–Ga single crystals and polycrystalline materials (Liu *et al.*, 2012). The magnetic shape memory (MSM) effect is based on the two following mechanisms: magnetically induced reorientation of martensitic variants and magnetically induced martensitic phase transformation (Liu *et al.*, 2012), the first one being the more common mechanism. A problem in MSMA is that a quite large magnetic field is required to induce the martensitic phase transformation. In real applications, it is not practical to use a superconducting magnet for actuation. As a consequence, instead of martensitic phase transformation, actuation due to reorientation of martensite variants is the most explored mechanism since a small magnetic field generated by a conventional magnet is enough for actuation. In this case, the shape recoverable strain is similar to that obtained by martensitic transformation, but the shape recovery force is small (around a few MPa).

In turn, embedding magnetic particles in shape memory matrices is also a promising approach to magnetically-actuate shape memory materials. In this way, the shape recovery of the material could be triggered without direct contact with a thermal source.

Magnetic shape memory reinforcement phase in a polymeric matrix

A common approach to obtain MSMCs is to embed micro/nanometer sized crystalline MSM particles in a matrix with similar stiffness so that the particles can deform while maintaining the coupling of the MSM particles with each other and the matrix. This ensures that, on one side, deformation of the composite will lead to stress-induced twin boundary motion in the SMS particles (e.g., for dampers) and, on the other side, magnetic field-induced twin boundary motion in the MSM particles will lead to a deformation in the composite (e.g., actuators) (Scheerbaum *et al.*, 2007).

The fabrication on 2000 of a Terfenol-D/polymeric matrix composite that exhibited magnetic-field induced strains of about 1000 ppm (Duenas and Carman, 2000) served as motivation to Feuchtwanger *et al.* to incorporate MSMA in a polymeric matrix (Hosoda *et al.*, 2004; Feuchtwanger *et al.*, 2003). Carman's group (Duenas and Carman, 2000) showed that by embedding a magnetostrictive material (Terfenol-D) in a polymeric matrix the brittleness of the active phase was not an issue when tested in tensile loading. Feuchtwanger *et al.* followed the same approach using Ni–Mn–Ga particles to produce composites that combine their ability to dissipate energy with a form that has a better performance under tension (Feuchtwanger *et al.*, 2003). Since then, many efforts have been devoted to the fabrication of polymer matrix MSMA composites with enhanced performance. A compilation of some of the most relevant polymer-based matrix MSMA systems reported so far are listed in Table 1. The morphology of the reinforcement phase ranges from particles to wires, ribbons and fibers.

Materials and synthesis

Different approaches can be followed to produce MSM fillers. The two most common types of morphologies (i.e., namely particles and wires) are shown in Fig. 1. To produce irregular-shaped particles a common approach is to synthesize them by mechanical ball-milling (Sun and Xie, 2010; Tian *et al.*, 2014; Liu *et al.*, 2010; Tian *et al.*, 2008) from a previously prepared polycrystalline

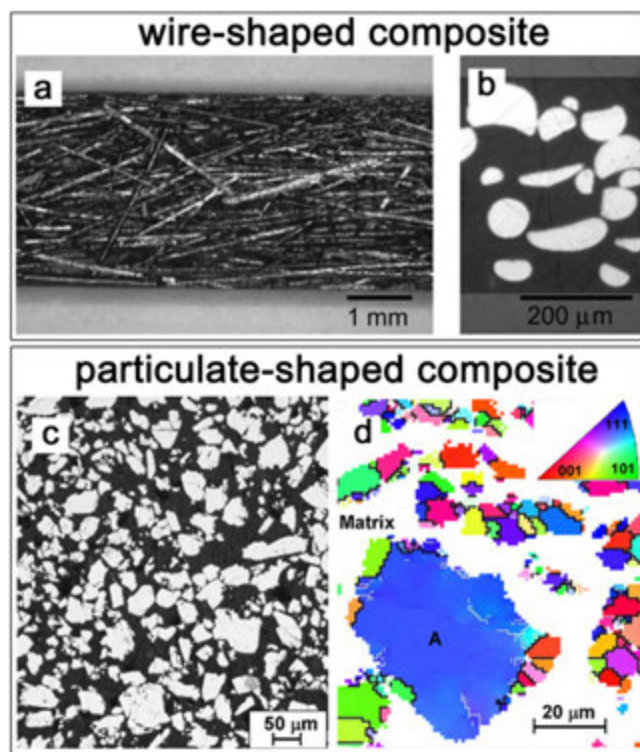


Fig. 1 Micrograph of the surface (a) and cross section (b) of a Ni–Mn–Ga wire-epoxy matrix. Top view micrograph (c) and normal direction (ND) inverse pole figure (IPF) map (d) of Ni–Co–Mn–In particulate-epoxy matrix composite. Reproduced with permission from (b) Glock, S., Zhang, X.X., Kucza, N.J., Müllner, P., Michaud, V., 2014. Structural, physical and damping properties of melt-spun Ni–Mn–Ga wire-epoxy composites. *Compos. Part A Appl. Sci. Manuf.* 63, 68–75. (d) Liu, D.M., *et al.*, 2010. In-situ studies of stress- and magnetic-field-induced phase transformation in a polymer-bonded Ni–Co–Mn–In composite. *Mater. Sci. Eng. A* 527 (15), 3561–3571.

ingot with the desired composition. After ball-milling, the particles are usually annealed to release internal stresses and to obtain the target structure. To ensure single crystalline powders, some authors start from single crystalline and columnar crystals cut by electron discharge machining into small pieces. The powders are later mechanically milled by ring mill and subsequently powder sieved to 150–300 μm diameter. To produce an oriented martensite twin structure, the annealed powders are sometimes inserted to a steel ring-mold in a rubber enclosure and compressed up to a stress of 3 MPa (Hannula *et al.*, 2012). In other studies, the particles are obtained by gently grinding annealed melt-extracted fibers of about 40–100 μm in diameter and several millimeters in length. Using this approach, single- or oligo-crystalline particles are obtained (Kauffmann-Weiss *et al.*, 2012). A different method relies in the use of spark erosion (Feuchtwanger *et al.*, 2018, 2005; Feuchtwanger, 2006). Spark erosion consists of placing electrodes of the desired metal in a liquid dielectric bath and pulsing a current across the electrodes. The electric discharge generates a plasma and melts or vaporizes a small amount of the electrode material. The dielectric material quenches the ejected material and spherical particles are formed in the liquid (Feuchtwanger, 2006). Using this method Feuchtwanger *et al.* (2018) produced mostly single crystals exhibiting a 10M martensitic structure from 20 to 100 μm. Wire-filled composites have been prepared by melt-spinning from an ingot with the desired composition (Glock *et al.*, 2014; Glock and Michaud, 2015). To produce the composite, the wires are placed and aligned in a specifically designed mold and mixed with the resin. Less common morphologies like 1–3 or 2–2 composites with platelets and fibrils are also produced by cutting monolithic Ni–Mn–Ga alloy with an electric discharge system (Gans and Carman, 2006).

Once the particles/fibers/wires are obtained, they are mixed with the selected polymer and cured at an appropriate temperature. In some cases, to obtain ordered composites, the mixture is cured under a magnetic field to let the filling phase align in columns with their crystallographic easy magnetization axis oriented along the field direction (Feuchtwanger *et al.*, 2005; Hannula *et al.*, 2012; Tian *et al.*, 2014, 2008). This method results in an easy magnetization behavior for the target direction and a harder magnetization behavior for the perpendicular directions (Kauffmann-Weiss *et al.*, 2012; Sratong-On *et al.*, 2019).

Applications

As can be observed in Table 1, Ni–Mn–Ga/polymer composites are the most explored composite systems because of their high damping capacity. The first studies on the use of Ni–Mn–Ga/polymer composites as energy absorbers were published by Feuchtwanger *et al.* (2003). The authors showed the ability of the composites to dissipate more energy than the matrix material and showed evidence that the composites had twin boundaries that could be moved by an external applied stress (Feuchtwanger

et al., 2003, 2005; Feuchtwanger, 2006). In the case of linear elastic materials, the amount of energy dissipated by the composites can be quantified by determining the ratio of the imaginary to the real part of the elastic modulus (Feuchtwanger *et al.*, 2005). For the non-linear elastic materials, the figure of merit (expressed as $E \cdot \tan\delta$, E being the stiffness) is commonly used to quantify the quality of materials as dampers.

Although the damping performance from the composites listed in Table 1 was measured using different characterization techniques (i.e., DMA, tension/compression test), all the materials studied in this review exhibit enhanced damping performance when compared to reference materials. For MSMA composites for damping applications, it is of prime importance the use of a polymeric matrix that matches the stiffness of the reinforcing MSM phase and the bonding between the matrix and the reinforcing phase. If the matrix is too rigid, the particles are constrained and cannot deform; on the contrary, if the matrix is too soft, the strain is not transferred from the matrix to the particles.

Hannula *et al.* (2012) reported a $E \cdot \tan\delta$ product of 3.5 GPa for a Ni–Mn–Ga/epoxy composite. This value is much higher than that of bulk single crystal 10M martensite (0.2 GPa) or rubber (0.004 GPa). In Table 1, the loss tangent ($\tan\delta$) of various composites measured under different conditions and equipment is listed. Remarkably, Feuchtwanger *et al.* (2005) reported a loss tangent of 1.138 for a Ni–Mn–Ga composite under an applied stress. This value is much higher than that reported for the unfilled polymer sample (0.119) and that reported for the Fe filled composite (0.737). In a later work, Feuchtwanger *et al.* (2018) compared the dynamic mechanical response of Ni–Mn–Ga/silicone composites using the same matrix and experimental conditions but varying the amount and type of ferromagnetic particles. They found that there was a minimum filling factor for Ni–Mn–Ga particles which affected the damping properties of the composites. The composites with 10 wt% of Ni–Mn–Ga particles did not exhibit any significant change in their damping behavior compared to the pure polymer; contrarily, the composites with 20 wt% of Ni–Mn–Ga particles showed a clear martensitic phase transformation visible in the storage modulus and loss angles, indicating that the particles actively participate in the energy dissipation process. They also found that spherical particles showed larger damping than irregular ones, while size and size distribution contributed less to the damping behavior.

Most of the works reported in the literature about MSMA explore the damping behavior compared to reference composites or pure polymeric materials but the comparison among different structures of shape memory fillers has been usually overlooked. Glock and Michaud (2015) studied the strain amplitude and frequency dependent damping behavior of Ni–Mn–Ga composites with a 10M and NM martensite and austenite embedded powders in a polymeric matrix. Below martensitic transformation temperature and glass transition temperature in the epoxy matrix, the temperature range of interest for damping applications, Glock *et al.* observed larger dissipative effects in the NM powder than in the 10M powder composite. In turn, the annealed martensitic Ni–Mn–Ga powder composite showed an increased damping behavior due to stress induced twin boundary motion in the Ni–Mn–Ga elements, compared to other reinforcements and to the pure matrix. At room temperature, the loss ratio of 10M martensite powder composite was 0.064, and the authors found that this value was about 1.6 times higher than that of a Cu–Ni composite (used as reference material) and about 1.9 times higher than that of low purity Ni–Mn–Ga powder composites with unknown crystal structure.

Regarding the actuation performance of Ni–Mn–Ga shape memory alloys, high MFIS up to 12% have been reported for non-modulated tetragonal martensite single crystalline alloys (Sozinov *et al.*, 2013). However, polycrystalline Ni–Mn–Ga alloys exhibit much lower MFIS (0.1%) due to grain boundary constraining twin boundary motion inside the grains. As previously mentioned, a possible approach to overcome the low actuation performance of MSMA is by embedding single or oligocrystalline particles in a polymeric matrix. Sratong-On *et al.* (2019) listed the prerequisites required to expect a large MFIS from a Ni–Mn–Ga/polymer composite: (1) individual particles should exhibit MFIS; (2) the use of a polymeric matrix that matches the stiffness of the reinforcing MSM phase; (3) an appropriate volume fraction of particles to prevent from blocking of particles deformation by neighboring particles; and (4) finally, spatially-controlled assembling of particles and their crystallographic orientation. Following the previous prerequisites, authors reported a Ni–Mn–Ga/silicone composite able to be deformed about 4% in elongation and – 2% in contraction (Fig. 2). In the magnetostrictive measurements of Fig. 2, a magnetic field, H , was applied perpendicular to the particles chains. When H reached a switching value, the embedded particles started to contract by rearranging their twin structure to align their short c -axis parallel to the field direction, whereas exhibiting a concurrent elongation in the orthogonal direction along the particles chains (Sratong-On *et al.*, 2019).

Although the most widely studied system among FSMAs is Ni–Mn–Ga, off-stoichiometric Ni–Mn–Z ($Z = \text{In, Sn, and Sb}$) metamagnetic shape memory alloys (MMSMAs), a relatively new type of MSMA in which the martensitic transformation temperature can be controlled by a magnetic field, has arisen as good candidates in actuator and sensor applications (Umetsu *et al.*, 2016). In MMSMA, the martensitic transformation occurs simultaneously with a magnetic phase change (i.e., the structural phase, for example, austenite, can be ferromagnetic while the other phase, martensite, can be paramagnetic or anti-ferromagnetic), and this structural phase change can be induced by stress fields repeatedly (Karaca *et al.*, 2009).

In this context, Ni–Co–Mn–In particles have been incorporated in a polymeric matrix to study its actuation performance. Liu *et al.* (2010) observed a reversible strain of 1.76% which was attributed to magnetic-field-induced reverse martensitic transformation in a pre-strained composite.

Recently, Barta and Karaman (2019) embedded $\text{Ni}_{43}\text{Co}_7\text{Mn}_{39}\text{Sn}_{11}$ MMSMA particles in an aluminum matrix. The idea behind the work was that the NiCoMnSn sensory particles would experience martensitic transformation (MT) in the presence of the crack tip stress field that would subsequently emit acoustic signals and would change their magnetic state upon the transformation. Authors demonstrated the feasibility of the sensory magnetic particle approach as a potential new structural health monitoring technique.

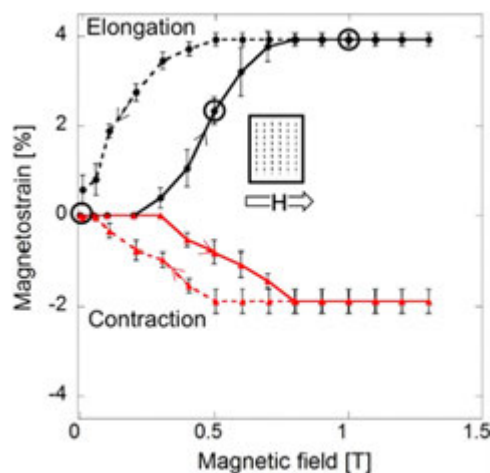


Fig. 2 Magnetic field-induced deformation of Ni–Mn–Ga particles/silicone composite optically measured using ImageJ program. Magnetostrain curves showing the sample contraction along the magnetic field accompanied by its elongation in the orthogonal direction. Dashed curves depict the strain recovery as the magnetic field removes. Reproduced with permission from Sratong-On, P., Chernenko, V.A., Feuchtwanger, J., Hosoda, H., 2019. Magnetic field-induced rubber-like behavior in Ni–Mn–Ga particles/polymer composite. *Sci. Rep.* 9 (1), 3443.

Magnetic particles in a shape memory polymeric matrix

Shape memory polymers (SMP) are by far the most widely used shape memory matrix materials to incorporate magnetic particles. SMPs have the ability to recover their original shape by the application of an external stimulus such as temperature, pH, light, electric or a magnetic field. They can also store and recover large strains in response to a stimulus. SMP are obtained by combining a physically or chemically cross-linked network structure that offers rubber elasticity and a switching element, i.e., a second type of cross-links that can be switched on or off under an external stimulus. This element, which is responsible for the shape fixity, is often created by means of phase separation, and a phase transition temperature (T_{trans}), which can either be a glass transition (T_g) or a melting temperature (T_m), is used as the switch. During the programming step, the material is heated and deformed at a switching temperature (T_s) above T_{trans} and is subsequently cooled below T_{trans} in order to fix the temporary shape. The original shape is restored when the sample is reheated above T_{trans} (Madbouly and Lendlein, 2009; Calvo-Correas *et al.*, 2019). SMP exhibit many advantages over conventional SMAs such as simplicity of processing and low cost. However, their low stiffness and consequently the weak recovery force after constrain can hamper their applicability in certain fields. One of the strategies to overcome this drawback relies on the addition of rigid fillers such as fibers. Furthermore, if the selected filler is magnetic, additional functional properties can be achieved. In particular, the application of an alternating magnetic field will generate a rapid and homogeneous heating effect without the need for direct contact with a thermal source thanks to the energy dissipated during rapid magnetization reversal (Soto *et al.*, 2018a). The inductive heating phenomena caused by the FM particles on the SMP matrix can be advantageous for various application fields. For instance, the incorporation of FM particles to a SMP device could eliminate power transmission lines (i.e., fiber optics, wires and their connections), more complex device shapes could be achieved as the particles can be homogeneously distributed in the matrix, SMP devices could be remotely activated or selective heating of an specific device area by selective area impregnation could be achieved (Buckley *et al.*, 2006).

Few works in the literature demonstrate the feasibility of SMP actuation by inductive heating by embedding a certain amount of ferromagnetic particles in SMP matrices (Soto *et al.*, 2018a; Buckley *et al.*, 2006; Petcharoen and Sirivat, 2016; Weigel *et al.*, 2009). Some of them are summarized in Table 2.

Materials and synthesis

Iron oxide particles are among the most widely used filler materials but NdFeB particles (Golbang and Kokabi, 2010) or nickel powders (Zhang *et al.*, 2010) have also been studied to thermomagnetically or electromagnetically induce shape memory effect. Fe_3O_4 particles are usually prepared following a co-precipitation method from aqueous $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution (Calvo-Correas *et al.*, 2019; Soto *et al.*, 2018a,b; Meiorin *et al.*, 2018; Puig *et al.*, 2012). Some authors also used commercial Fe_3O_4 spherical particles (Yakacki *et al.*, 2009). To enhance the compatibility with the SMP matrix, filler materials are usually treated. Silica (Weigel *et al.*, 2009) and oleic acid (Meiorin *et al.*, 2018; Puig *et al.*, 2012; Yang *et al.*, 2012) coatings or silane coupling agent treatment (Zhang *et al.*, 2010, 2009) have been widely used to coat ferromagnetic fillers (i.e., Fe_3O_4 , Ni).

Concerning SMP matrices, one of the most commonly used polymeric matrix materials are segmented polyurethanes (PUs) as their shape-memory properties can be activated by heating, show excellent chemical stability and potential biocompatibility and biodegradability (Soto *et al.*, 2018b). Recent studies also used bio-based polyurethane as the matrix phase which leads to an “inversion” of the role of phases from the commonly used segmented thermoplastic PU where the phase formed by macrodiol acted as the hard phase while the phase constituted by the diisocyanate and chain extender is used as the switching element. The synthesis of bio-based PU, besides the interest to use PU derivatives from renewable sources for economic, environmental and social

Table 2 Magnetic reinforcements in shape memory polymeric matrices

Magnetic reinforcement	Reinforcement type	SMP matrix	Results	Ref.
Fe ₃ O ₄	Nanoparticles	PU (segmented or bio-based)	Shape recovery via magnetic NP heating	(Calvo-Correas <i>et al.</i> , 2019; Soto <i>et al.</i> , 2018a,b; Calvo-Correas <i>et al.</i> , 2016)
Iron oxide	~ 9.8 nm nanoparticles	Tung oil/styrene	Shape recovery via magnetic NP heating	(Meiorin <i>et al.</i> , 2018)
Carbonyl iron (CIPs)	Particles	Poly(ethylene glycol) dimethacrylate (PEGDMA)	T _g can be controlled by the composites' structure and by the content of magnetic particles	(Hassan <i>et al.</i> , 2018)
Magneto-rheological	Fluid	Poly(dimethylsiloxane)	High stiffening under a magnetic field and fast and fully reversible magnetic shape memory.	(Testa <i>et al.</i> , 2019)
Fe	Microparticles	Shape memory thermoplastic PU thin film (DiAPLEX MM5520)	Composite films that simultaneously respond to magnetic fields and light	(Liu <i>et al.</i> , 2019)
Fe ₃ O ₄	~ 11 nm nanoparticles	Oligo(ϵ -caprolactone)dimethacrylate/butyl acrylate	SM effect activated by a touchless and highly selective electromagnetic stimulus	(Schmidt, 2006)
Fe ₃ O ₄	Nanoparticles	Methacrylate-based thermoset SMP networks	Systematical study about the correlation between polymer crosslinking and magnetic NP on polymerization, mechanical, thermomechanical and SM properties	(Yackacki <i>et al.</i> , 2009)
NdFeB	Particles	Crosslinked low density polyethylene (XLDP)	Electromagnetically triggered shape memory properties using an alternative magnetic field. The sample containing 15wt% NdFeB reached a full shape recovery of 25% extension within 6 minutes	(Golbang and Kokabi, 2010)
Ni	Powder	Styrene copolymer	Effect of surface Ni treatment on magnetic behavior of SMPC and elongation under magnetic field	(Zhang <i>et al.</i> , 2010)
Multiwalled carbon nanotubes coated with Fe ₃ O ₄ nanoparticles	Nanoparticles	Poly(ϵ -caprolactone) (PCL) nanofibers	Excellent magnetic-active shape memory effect in electrospun nanofibers. The nanofibers and their degradation products showed good biocompatibility	(Gong <i>et al.</i> , 2012)

concerns, also provides the advantage that they do not produce adverse tissue reactions and their degradation products are considered non-toxic (Bruin *et al.*, 1990). For instance, non-toxic behavior, good hemocompatibility, and cell adhesion of magnetite-loaded bionanocomposites were reported by Calvo-Correas *et al.* (2019). Unsaturated vegetable oils (e.g., tung oil, modified linseed oil) and derived reactive monomers can also exhibit shape memory behavior and have arisen as promising bio-based polymeric matrix materials (Meiorin *et al.*, 2018).

To prepare Fe₃O₄-filled PU nanocomposites, PU pellets can be dissolved in dimethylformamide (DMF) and then mixed with the desired amount of particles. The polymeric matrix can also be obtained by monomers mixture and the use of a cationic reaction initiator (Meiorin *et al.*, 2018; Yackacki *et al.*, 2009). Ultrasounds are commonly utilized to obtain stable and homogeneous suspensions (Soto *et al.*, 2018a,b). The final composite can be prepared by solvent casting of the final suspension followed by curing and drying (Soto *et al.*, 2018a,b). Also, the resulting films can be compression molded in a hot-press (Calvo-Correas *et al.*, 2019).

Applications

Remotely heated shape memory materials are very appealing for biomedical applications. In particular, the ability of magnetic nanoparticles to develop heat energy locally and selectively is a topic of interest for their use in tumor therapy and in hot melt glues that can be cured by microwaves (Yackacki *et al.*, 2009; Bruin *et al.*, 1990).

Meiorin *et al.* (2018) investigated the effect of the loading of iron oxide nanoparticles in a polymeric matrix with high bio-based content and their magnetic remote activation of shape recovery. The morphology of the composite is depicted in Fig. 3(a). Their results showed that all the nanocomposites presented superparamagnetic behavior at room temperature and that the agglomeration increased with MNP content. The shape recovery process was magnetically activated, and the permanent original shape was recovered. As shown in Fig. 4(a), the sample with 10 wt% MNP presented the best heating behavior with the shortest time for shape recovery. In Fig. 4(b), the first and last images correspond to images without applied field, where the blue color correspond to lower temperature values. The sequence clearly shows the gradual and desired homogenous heating of the sample. Hence, these composites are valuable materials for applications such as sensors and actuators.

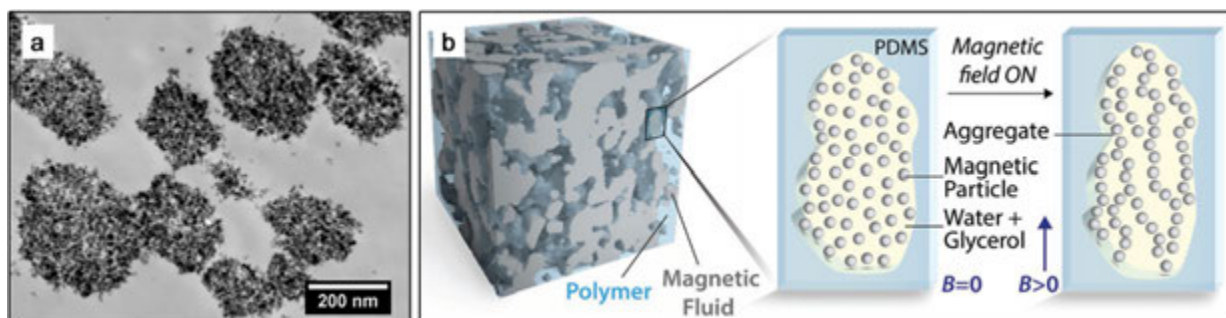


Fig. 3 (a) STEM image of a lamella prepared by ultramicrotomy for a magnetite particles embedded in tung oil/styrene matrix. (b) 3D reconstruction of a polymer/magneto-rheological fluid composite. The effect of the magnetic field on the internal structure of the magnetic phase in a droplet is also shown. Reproduced with permission from (a) Meiorin, C., Actis, D.G., Montoro, F.E., *et al.*, 2018. Magnetic remote activation of shape recovery in nanocomposites based on tung oil and styrene. *Phys. Status Solidi* 215 (24), 1800311. (b) Testa, P., Style, R.W., Cui, J., *et al.*, 2019. Magnetically addressable shape-memory and stiffening in a composite elastomer. *Adv. Mater.* 31 (29), 1900561.

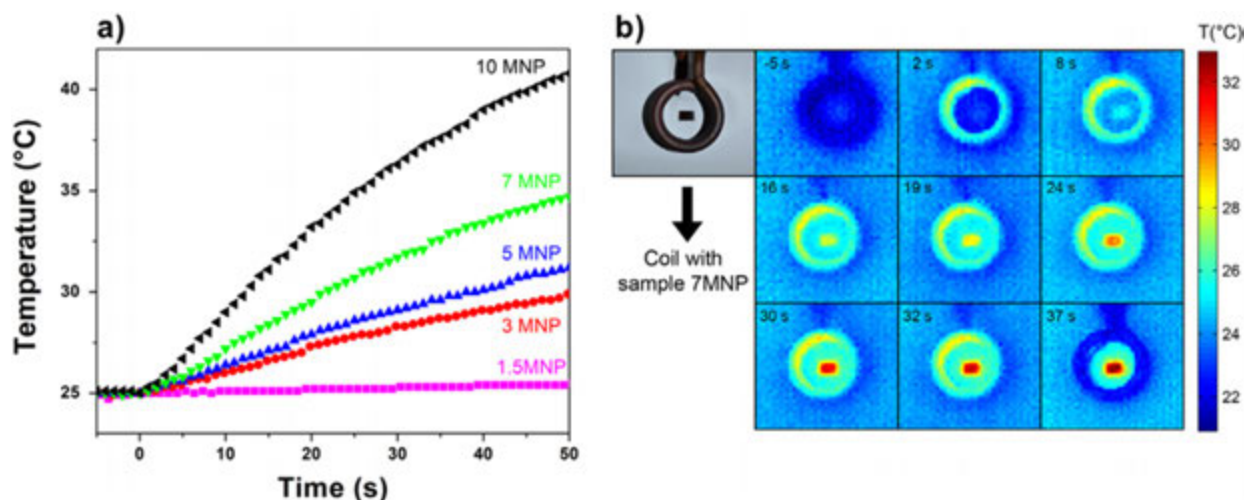


Fig. 4 (a) First 50s of the magnetothermal measurements for nanocomposites with different content of MNP under application of an alternating magnetic field turned on at 0 s. (b) Series of images taken with a thermographic camera at different times (the field was turned on at 0 s and turned off at 36 s). Reproduced with permission from Meiorin, C., Actis, D.G., Montoro, F.E., *et al.*, 2018. Magnetic remote activation of shape recovery in nanocomposites based on tung oil and styrene. *Phys. Status Solidi* 215 (24), 1800311.

Hassan *et al.* (2018) fabricated novel functionally graded magnetic SMPs using carbonyl iron particles embedded into a polymeric matrix by a three-dimensional printing technique. The authors observed that T_g could be controlled along the graded structure as well as the filler content of the magnetic particles. The obtained results strongly support the remote controllability of the material properties for magnetically responsive material applications.

A novel approach to obtain soft magnetic shape-memory composite has been recently reported by Testa *et al.* (2019). Authors encased liquid droplets of magneto-rheological fluid into a poly(dimethylsiloxane) (PDMS) matrix (Fig. 3(b)). The advantages of these novel composites rely in the larger mobility of the particles when suspended in a liquid solvent that cause the mechanical changes to be more effective, resulting in a larger stiffening effect. The liquid nature of the magnetic component also avoids the reduced durability and embrittlement typically associated to hard particles. This new type of composite exhibits an almost 30-fold increase in shear modulus under a magnetic field which results in a fast and fully reversible magnetic shape-memory by three different ways, namely embossing, simple shear and unconstrained 3D deformation (Testa *et al.*, 2019).

The use of magnetic shape memory composites in the field of soft robotics has been recently explored by Liu *et al.* (2019) with the development of a composite of magnetic iron microparticles dispersed in a shape memory polymer matrix. In their work, the composites are used in a bifunctional manner for simultaneous magnetic actuation and photothermal heating. In practice, they are used as soft robotic devices that can be shaped in the form of cantilevers, flowers, spirals or grabbers. In these composites, magnetic fields are used to set temporary shapes while illuminating the composite to drive photothermal heating and reduce the elastic modulus of the SMP. The temporary shape can be repeatedly locked and then subsequently unlocked and reconfigured. The device can be further programmed by also modifying the permanent shape.

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Modeling the Behavior of Shape Memory Alloys and Memory Alloy-Based Devices

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Nomenclature

A_{0f}	Austenite finish temperature in absence of stress [K]	M_f	Martensite finish temperature [K]
A_{0s}	Austenite start temperature in absence of stress [K]	M_s	Martensite start temperature [K]
A_f	Austenite finish temperature [K]	T_{ref}	Reference temperature of the SMA [K]
A_s	Austenite start temperature [K]	α_A	Thermal expansion coefficient of the Austenite phase [1/K]
C_A	Stress rate of the Austenite phase [MPa/K]	α_M	Thermal expansion coefficient of the Martensite phase [1/K]
C_M	Stress rate of the Martensite phase [MPa/K]	ε_l	Maximum recoverable strain of the SMA [mm/mm]
E_A	Elastic modulus of the Austenite phase [GPa]	ν_A	Poisson's ratio of the Austenite phase [–]
E_M	Elastic modulus of the Martensite phase [GPa]	ν_M	Poisson's ratio of the Martensite phase [–]
G_A	Shear modulus of the Austenite phase [GPa]	ξ	Martensite volume fraction [–]
G_M	Shear modulus of the Martensite phase [GPa]	σ_{fcr}	Martensite finish critical stress [MPa]
M_{0f}	Martensite finish temperature in absence of stress [K]	σ_{scr}	Martensite start critical stress [MPa]
M_{0s}	Martensite start temperature in absence of stress [K]		

Glossary

Austenite One of the phase of the Shape Memory Alloys, which is stable at low stress and high temperature.

Martensite One of the phase of the Shape Memory Alloys, which is stable at high stress and low temperature.

NiTiNOL An alloy composed of Nickel and Titanium. The word NiTiNOL is referred to its composition (Nickel and Titanium) and place of discovery (Naval Ordnance

Laboratory). NiTiNOL is one of the most used Shape Memory Alloys.

Shape Memory Alloy (SMA) An alloy that can return (“remember”) to its original shape, after a deformation has occurred, when heated.

UMAT User defined Material, subroutine of the Abaqus finite element code. It allows to define a material whose behavior is not originally available in the Abaqus material library.

Introduction

In the last decades, the interest towards Shape Memory Alloys (SMA) is unquestionably increasing, thanks to their peculiar properties such as pseudo-elastic behavior and Shape Memory Effect (SME). Indeed, their behavior, combined with their high power-to-weight ratio (Sellitto and Riccio, 2019), makes them particularly suitable for the design of actuators (Mohd Jani *et al.*, 2014) and adaptive structures (Thill *et al.*, 2008). Moreover, SMA-based actuators promise benefits in terms of weight and complexity reduction respect to traditional hydraulic and electric actuation systems (Tzou *et al.*, 2004; Neugebauer *et al.*, 2010). Among them, NiTiNOL is one of the most used and investigated SMAs (Duerig *et al.*, 1999; Hartl *et al.*, 2010; Hartl and Lagoudas, 2007; Buehler and Wang, 1968). Several authors investigated the SMA behavior from an analytical, numerical, or experimental perspective.

In Baz *et al.* (2000), a mathematical model is presented, able to describe the behavior of NiTiNOL-reinforced composite beams by considering the interaction between the thermally induced shape memory effect of the NiTiNOL components and the elastic characteristics of the composite beams.

The elastodynamic response of thick SMA composite beams was investigated in Ghomshei *et al.* (2005). A higher-order shear-deformation beam theory and the von Karman strain field were used to simulate the behavior of the composite beams, while the thermo-mechanical characteristics of the SMA layers were modeled by using a one-dimensional constitutive model and sinusoidal phase transformation kinetics.

A constitutive model able to simulate the phase transformation in polycrystalline SMAs, based on a general thermodynamical description, is presented in Lagoudas *et al.* (2012). The model was validated by comparisons with experiments considering different thermomechanical paths, including thermally- and stress-induced transformations under various loads.

The thermomechanical model of polycrystalline SMAs is investigated in a series of works (Lagoudas and Bo, 1999; Bo and Lagoudas, 1999a,b,c). A generic form of Gibbs free energy was obtained by considering the polycrystalline SMA as a composite with evolving microstructure (Bo and Lagoudas, 1999a). Then, the first law of thermodynamics was introduced to derive the energy balance equation describing the heat exchange during the phase transformation (Lagoudas and Bo, 1999). Experimental tests on NiTi SMA wires undergoing thermal-induced phase transformation were introduced to validate the developed material constitutive model, by considering constant (Lagoudas and Bo, 1999) and cyclic (Bo and Lagoudas, 1999b) applied loads. In the last paper of the series (Bo and Lagoudas, 1999c), minor hysteresis loop was included in the constitutive model.

A numerical analysis on a SMA-based biomimetic active hydrofoil is presented in [Gamer *et al.* \(2000\)](#). SMA training and material characterization was discussed and used to introduce a thermomechanical constitutive model to numerically simulate the SMA behavior.

In [Haghdoust *et al.* \(2018\)](#), a SMA numerical constitutive model was introduced and validated by comparisons with experimental hysteresis loops at different maximum strain amplitudes. The introduced constitutive model considered the non-linear damping behavior of martensitic SMAs by using a modified version of Masing's rules.

A SMA material constitutive model, able to reproduce the SMA super-elastic behavior by taking into account the austenite-martensite phase transformation, is introduced in [Hu \(2014\)](#). Experimental tests based on cyclic loading were used to calibrate the numerical model.

The behavior of a composite beam actuated by SMA wires is numerically and experimentally investigated in [Icardi \(2001\)](#). A numerical procedure, based on the updated Lagrangian formulation, was introduced, able to consider the non-linearity of the composite beam and the hysteresis of the SMA wires.

In [Roh *et al.* \(2006\)](#), the thermomechanical behavior of SMA actuators was investigated and numerically simulated by using a 3D user defined material model implemented in the Abaqus Finite Element (FE) code (UMAT). The UMAT was applied to analyze SMA strips taking into account the pseudo-elastic behavior and the shape memory effect.

An overview on five large-scale SMA-based Boeing research programs is presented in [Calkins and Mabe \(2010\)](#). The programs aimed to demonstrate the feasibility of Nitinol-based devices in several aeronautical applications, such as variable engine inlet, reconfigurable rotor blade, variable geometry chevron, deployable and retractable rotor tab, and variable geometry fan nozzle. In [Sofla *et al.* \(2010\)](#), the activities related to the conceptual design, the prototype fabrication, and the evaluation of shape morphing wing were proposed. In particular, the authors investigated on the solutions based on SMAs. A shape adaptive mechanism, based on SMAs, was investigated in [Karakalas *et al.* \(2019\)](#), aimed to morph a wind turbine airfoil section to reduce the acting structural loads, while in [Manzo *et al.* \(2005\)](#) a flexible UAV wing, actuated by means of Flexinol wires, was experimentally investigated.

In [Brailovski *et al.* \(2008\)](#), [Georges *et al.* \(2009\)](#), the design of a morphing wing composed of flexible extrados, rigid intrados, and an actuator group located inside the wing box was presented. The actuator groups are composed of two individually controlled SMA actuators.

Moreover, several solutions can be found in the literature, inspired by the biology ([Lazos, 2005](#); [Han *et al.*, 2016](#); [Colorado *et al.*, 2012](#); [Muhammad *et al.*, 2010](#)). In, ([Colorado *et al.*, 2012](#)) a micro aerial vehicle with actuated morphing wings able to mimic the movements of a bat is presented. NiTi SMAs were used as artificial biceps and triceps muscles. In [Muhammad *et al.* \(2010\)](#), composite plates and aluminum rivets were used to mimic the bending zone of a beetle hind wing. Electrically-activated SMA wires were used to trigger the folding and unfolding operations.

Finally, different applications of SMA-based actuators can be found in the literature ([Grigorie *et al.*, 2012a,b](#); [Kang *et al.*, 2012](#)), aimed to modify a wing geometry. The actuation is obtained by heating the SMA wires by means of an applied electric current. Usually, in this kind of application, the SMA actuators remain in their actuated configuration as long as the electric current is applied. However, this lead to high thermal and mechanical overstresses in the SMA components. To reduce the latter, while simultaneously assuring a reduction of the energy consumed due to the actuation, bi-stable devices are being investigated ([Hochstein, 1985](#); [Morgen and Yee, 1999](#); [Luchetti *et al.*, 2009](#)). These devices are characterized by two stable actuated and de-actuated energy-free configurations, which do not require any external energy to be kept in an actuated state.

This work is focused on the development of a constitutive material model able to reproduce the complex behavior of the SMA. UMAT subroutines have been implemented in the Abaqus FE standard environment, able to take into account the SMA pseudo-elastic behavior and the shape memory effect. Analytical models available in the literature have been used to validated the UMAT. Then, the mechanical behavior of the bi-stable SMA-based actuator, developed and preliminary introduced in [Saputo *et al.* \(2019\)](#), has been further investigated by numerical analyzes performed with the support of the implemented UMAT subroutines.

In Section "Theoretical Background: Shape Memory Alloys", a theoretical background on SMAs is introduced. In Section "Numerical Implementation of the SMA Behavior", the material model implemented in the UMAT is presented; while, in Section "SMA-Based Actuators", the main characteristics of SMA-based actuators are detailed. In Section "Feasibility Study on a bi-stable biased SMA Actuator", the developed bi-stable device is introduced and the numerical results are assessed. Finally, in Section "Pros and Cons of the Proposed Approach", Pros and Cons of the proposed approach are briefly introduced.

Theoretical Background: Shape Memory Alloys

The key characteristic of SMAs is their capability to shift between two distinct crystalline phases:

- (1) The Austenite "parent" phase, which is stable at low stress and high temperature;
- (2) The Martensite "daughter" phase (which can be divided in twinned and detwinned), which is stable at high stress and low temperature ([Suzuki and Wuttig, 1972](#)).

Fig. 1 shows the Austenite and Martensite phases of a NiTi SMA.

The Martensite transformation is diffusionless, meaning that it is formed from its parent phase by moving the atoms over a distance lower than the interatomic one.

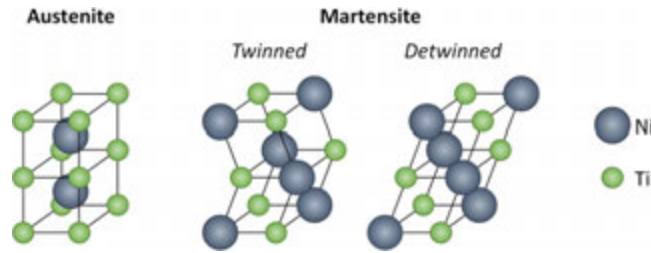


Fig. 1 Austenite and Martensite crystal phases.

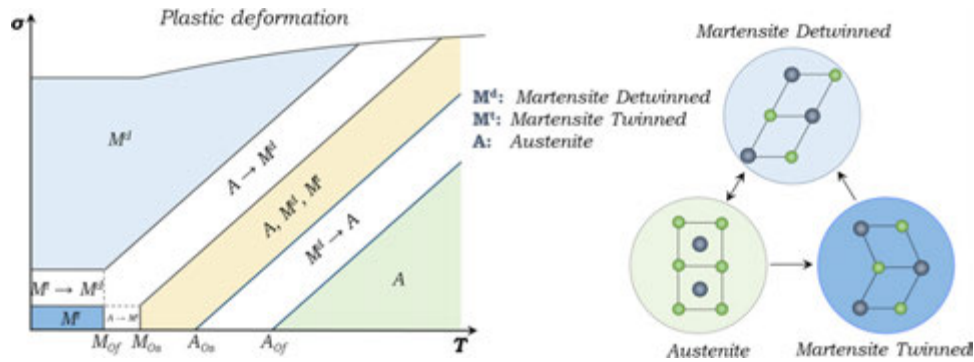


Fig. 2 SMA phase diagram.

The Austenite crystal structure is Body Centered Cubic (BCC): one Nickel atom is placed at the center of the crystallographic cube, while Titanium atoms can be found at the eight corners of the cube. On the other side, the Martensite lattice structure is characterized by a rhombus shape with an atom at each corner.

The Austenite and Martensite mechanical properties are typically very different; therefore, the transition between the phases strongly influences the behavior of the SMAs. Indeed, the particular combination of temperature and stress can result in one of the SMA phases, according to the phase diagram reported in [Fig. 2](#).

According to [Fig. 2](#), the characteristic temperatures Martensite start and finish, and Austenite start and finish, evaluated in absence of stress, are indicated respectively as M_{os} , M_{of} , A_{os} , and A_{of} . Additionally, different regions can be identified. In particular, the combination of low temperatures and high stresses results in a Martensite Twinned (M^t) or Detwinned (M^d) phase of the material. On the other hand, the Austenite (A) phase is induced by a combination of low stresses and high temperatures. Moreover, an intermediate region can be identified, in which the alloy can be found both in the Austenite or Martensite phases (A , M^t , M^d). The transition between phases can occur in the transition regions ($A \rightarrow M^d$, $A \rightarrow M^t$, $M^t \rightarrow M^d$, $M^d \rightarrow A$). Finally, high level of stress results in non-recoverable plastic deformations. Modifications of the stress and/or of the temperature field of the alloy can result in one of the most interesting characteristics of the SMAs, which are the pseudo-elastic behavior or the shape memory effect, described respectively in [Figs. 3](#) and [4](#).

According to [Fig. 3\(a\)](#), a temperature T_{ref} above the Austenite transformation temperature in absence of stress A_{of} is considered. Hence, the combination of stress and temperature results in an Austenite phase of the material. An increase in the stress at a constant temperature is then supposed. Therefore, the stress addition leads to the phase transition from the Austenite to the Martensite phase, leading to a variation of the mechanical properties of the alloy. Then, the stress is removed ([Fig. 3\(b\)](#)), resulting in the reverse transition from the Martensite to the Austenite phase. According to the stress-strain diagram in [Fig. 3\(b\)](#), no residual strain can be observed due to the pseudo-elastic behavior of the SMA.

In [Fig. 4](#), the Shape Memory Effect is described. In this case, a reference temperature T_{ref} below the Austenite start transformation temperature in absence of stress A_{os} is considered. The material is supposed initially in its Austenite phase. According to [Fig. 4\(a\)](#), the stress is progressively increased, resulting in the transition from the Austenite to the Martensite phase. Then, when the stress is removed ([Fig. 4\(b\)](#)), no phase transition from Martensite to Austenite occurs. Hence, in this case, the residual strain reported in the stress-strain diagram of [Fig. 4\(b\)](#) can be observed. However, this residual strain can be removed by increasing the temperature, which induce the Martensite to the Austenite phase transition shown in [Fig. 4\(c\)](#).

Numerical Implementation of the SMA Behavior

A user defined material subroutine has been implemented in the Abaqus FE environment, to numerically simulate the SMA pseudo-elastic behavior and shape memory effect. In the UMAT implementation, the simplified phase diagram reported in [Fig. 5](#) has been considered.

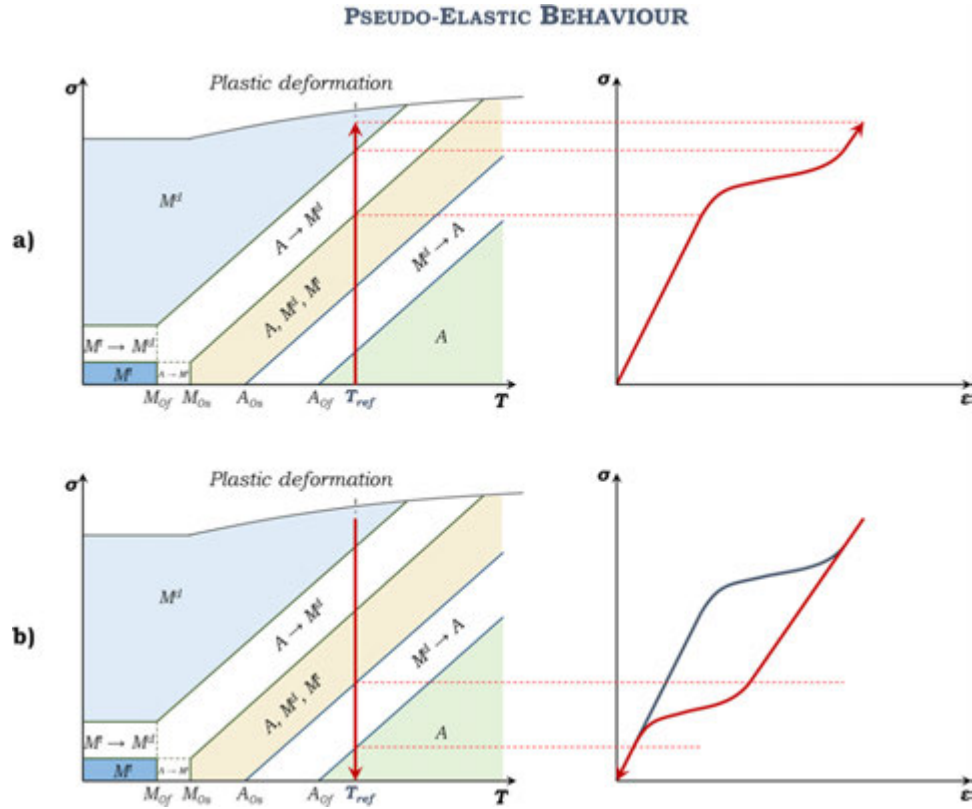


Fig. 3 Pseudo-Elastic behavior. (a) increase in the stress: stress-induced Austenite to Martensite phase transition; (b) decrease in the stress: stress-induced Martensite to Austenite phase transition.

According to the simplified phase diagram shown in Fig. 5, the parameters needed to define the SMA behavior are the Martensite start (M_s) and finish (M_f) temperatures, the Austenite start (A_s) and finish (A_f) temperatures, the Martensite start (σ_{scr}) and finish (σ_{fcr}) critical stress, and the stress rate (or stress influence coefficient) for the Austenite (C_A) and Martensite (C_M) phases.

Three UMAT sub-routines have been implemented according to the specific problem: UMAT 1D, UMAT 2D, and UMAT 3D. All the implemented subroutines share the same described procedure. In particular, it can be seen as a sequence of consecutive operations performed in the frame of three moduli. As an example, the procedure for the implementation of the UMAT 3D is described below.

In the first modulus, the material properties and the stiffness matrix of the alloy are calculated. In Eqs. (1) and (2), the compliance matrix of the Austenite and Martensite phases are respectively computed:

$$[S_A] = \begin{bmatrix} \frac{1}{E_A} & -\frac{\nu_A}{E_A} & -\frac{\nu_A}{E_A} & 0 & 0 & 0 \\ -\frac{\nu_A}{E_A} & \frac{1}{E_A} & -\frac{\nu_A}{E_A} & 0 & 0 & 0 \\ -\frac{\nu_A}{E_A} & -\frac{\nu_A}{E_A} & \frac{1}{E_A} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G_A} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G_A} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G_A} \end{bmatrix} \quad (1)$$

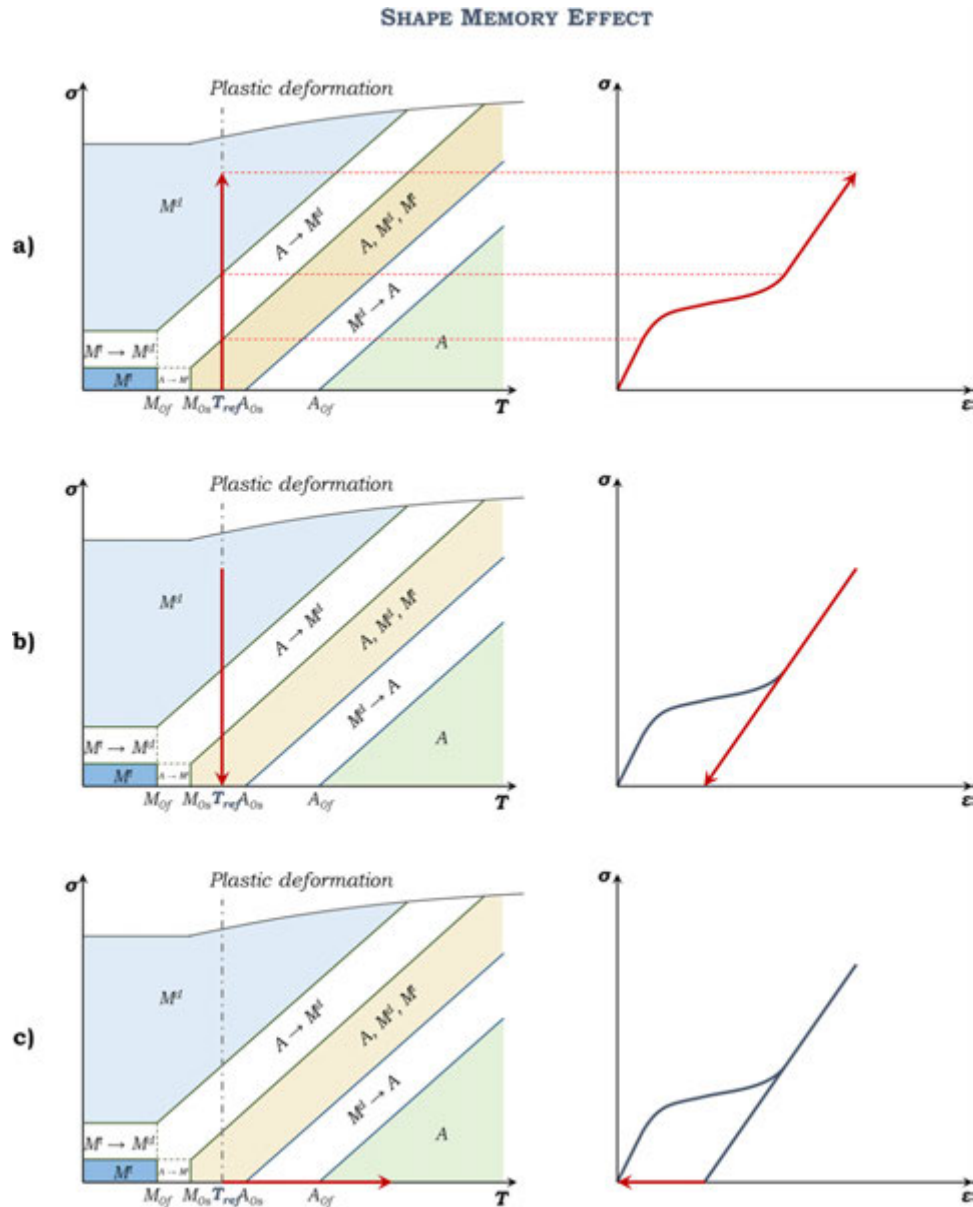


Fig. 4 Shape Memory Effect. (a) increase in the stress: stress-induced Austenite to Martensite phase transition; (b) decrease in the stress: no transition occurred; (c) increase in the temperature: temperature-induced Martensite to Austenite phase transition.

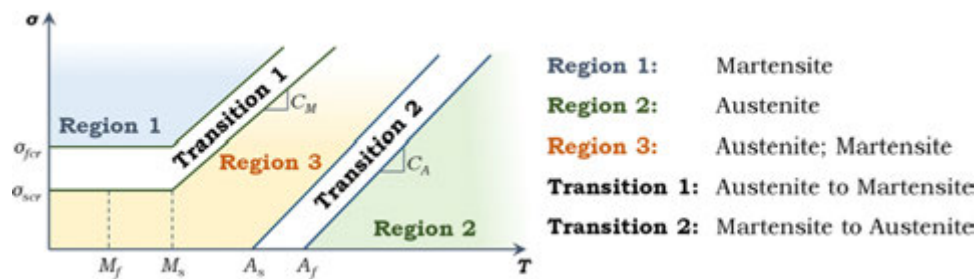


Fig. 5 Simplified phase diagram.

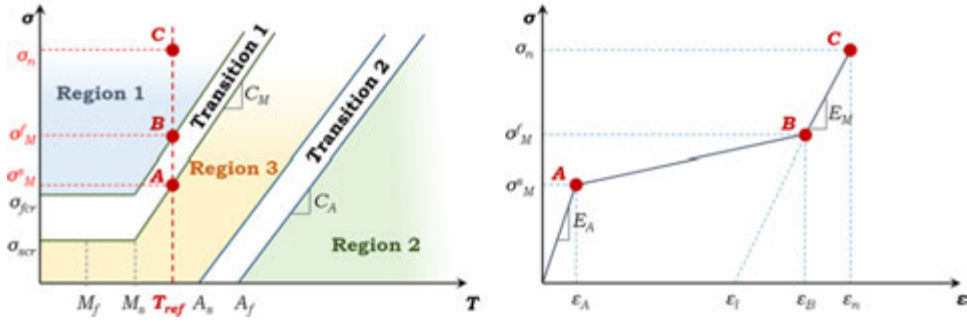


Fig. 6 Phase diagram and stress strain relationship: $T_{ref} < A_s$.

$$[S_M] = \begin{bmatrix} \frac{1}{E_M} & -\frac{\nu_M}{E_M} & -\frac{\nu_M}{E_M} & 0 & 0 & 0 \\ -\frac{\nu_M}{E_M} & \frac{1}{E_M} & -\frac{\nu_M}{E_M} & 0 & 0 & 0 \\ -\frac{\nu_M}{E_M} & -\frac{\nu_M}{E_M} & \frac{1}{E_M} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G_M} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G_M} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G_M} \end{bmatrix} \quad (2)$$

where E_A , ν_A , G_A , E_M , ν_M , and G_M are the elastic modulus, the Poisson's ratio, and the shear modulus of the Austenite and Martensite phases, respectively. Then, the compliance matrix of the element is computed as a function of the compliance matrix of the Austenite and Martensite phases and of the martensitic volume fraction ξ :

$$[S] = \xi[S_M] + (1 - \xi)[S_A] \quad (3)$$

In the second modulus, the stress-strain relationship is derived starting from the SMA phase diagram. Two different cases are considered, according to the reference temperature value T_{ref} .

In the first case, the reference Temperature T_{ref} is below the Austenite start transformation temperature A_s , as shown in Fig. 6.

According to Fig. 6, it is possible to derive the characteristic points A and B of the stress-strain relationship from the phase diagram. Hence, if the temperature T_{ref} is below the Martensite start transformation temperature M_s , the martensite start transformation stress σ_M^s , corresponding to the point A, and the martensite finish transformation stress σ_M^f , corresponding to the point B, are evaluated according to Eqs. (4) and (5):

$$\sigma_M^s = \sigma_{scr} \quad (4)$$

$$\sigma_M^f = \sigma_{scr} \quad (5)$$

Otherwise, if $M_s < T_{ref} < A_s$, Eqs. (6) and (7) must be defined:

$$\sigma_M^s = \sigma_{scr} + C_M(T_{ref} - M_s) \quad (6)$$

$$\sigma_M^f = \sigma_{scr} + C_M(T_{ref} - M_s) \quad (7)$$

Then, Eqs. (8) and (9) are introduced to compute the corresponding strains ϵ_A and ϵ_B , as a function of the elastic properties of the austenite and martensite phases:

$$\epsilon_A = \frac{\sigma_M^s}{E_A} \quad (8)$$

$$\epsilon_B = \frac{\sigma_M^f}{E_M} + \epsilon_l \quad (9)$$

where ϵ_l is the maximum recoverable strain.

In the second case, a reference temperature T_{ref} above the Austenite finish transformation temperature A_f is considered, as shown in Fig. 7.

The characteristic points A, B, D, and E are needed to define the stress-strain relationship shown in Fig. 7. Eqs. (6) and (7), used to evaluate the Martensite start transformation stress σ_M^s (point A) and the Martensite finish transformation stress σ_M^f (point B), still hold. Then, Eqs. (10) and (11) are introduced to evaluate the Austenite start transformation stress σ_A^s (point D) and the Austenite finish transformation stress σ_A^f (point E),

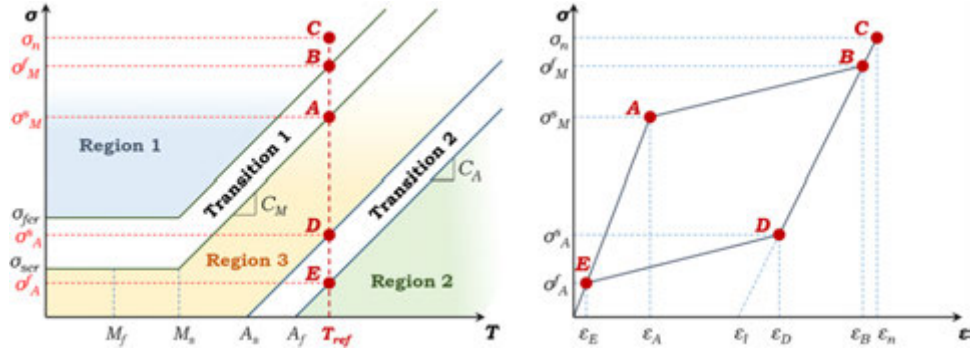


Fig. 7 Phase diagram and stress strain relationship: $T_{ref} > A_f$.

$$\sigma_A^s = C_A(T_{ref} - A_s) \quad (10)$$

$$\sigma_A^f = C_A(T_{ref} - A_f) \quad (11)$$

Finally, the corresponding strains ε_A and ε_{B_r} are computed by means of the previously introduced Eqs. (8) and (9), while Eqs. (12) and (13) are used to compute the ε_D and ε_E strains:

$$\varepsilon_D = \frac{\sigma_A^s}{E_M} + \varepsilon_l \quad (12)$$

$$\varepsilon_E = \frac{\sigma_A^f}{E_A} \quad (13)$$

Finally, in the third modulus, the strain and the stress of the whole model are updated by taking into account the temperature variation. Hence, the thermal matrix of the element $[K_T]$ is given by Eq. (14):

$$[K_T] = \xi[K_M] + (1 - \xi)[K_A] \quad (14)$$

where $[K_A]$ and $[K_M]$ are respectively the thermal matrix of the Austenite and Martensite phases:

$$[K_A] = \begin{bmatrix} \frac{\alpha_A E_A}{1 - 2\nu_A} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{\alpha_A E_A}{1 - 2\nu_A} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\alpha_A E_A}{1 - 2\nu_A} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (15)$$

$$[K_M] = \begin{bmatrix} \frac{\alpha_M E_M}{1 - 2\nu_M} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{\alpha_M E_M}{1 - 2\nu_M} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\alpha_M E_M}{1 - 2\nu_M} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (16)$$

According to Eqs. (15) and (16), α_A and α_M are the austenite and martensite thermal expansion coefficients.

The current compliance matrix $[S]$ is updated according to Eq. (17):

$$[S] = [S] + [dS] \quad (17)$$

In particular, $[dS]$ is the increment of the compliance matrix, given by:

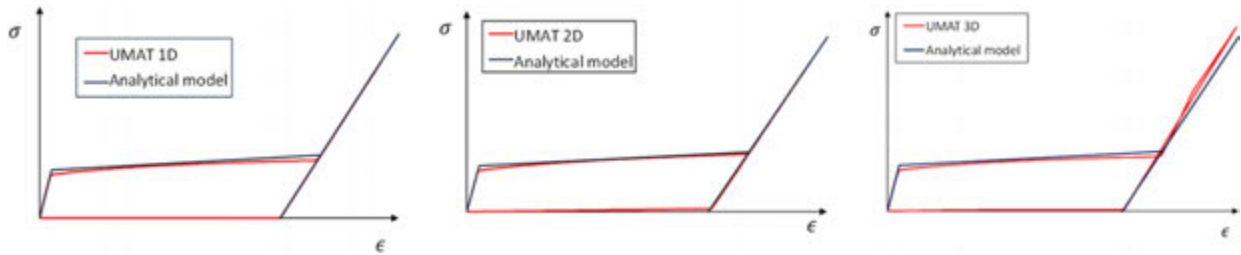
$$[dS] = [dS_M] + [K_T](T_1 - T_{ref}) + [dK_T](T_1 - T_0) \quad (18)$$

where $[dS_M]$ is the increment of the compliance matrix due only to the mechanical behavior, T_1 is the temperature of the current step, T_0 is the temperature of the previous step, and $[dK_T]$ is the increment of the thermal matrix, which is in turn a function of the increment of the martensite volume fraction $d\xi$ due to the thermal variation:

$$[dK_T] = d\xi([K_M] - [K_A]) \quad (19)$$

Table 1 NiTiNOL material properties

<i>NiTiNOL properties</i>		
σ_{scr}	[MPa]	100
σ_{fcr}	[MPa]	170
E_A	[GPa]	67
E_M	[GPa]	26.3
ν_A	[-]	0.33
ν_M	[-]	0.33
ε_f	[mm/mm]	0.067
C_A	[MPa/K]	13.8
C_M	[MPa/K]	8
α_A	[1/K]	2.2×10^{-6}
α_M	[1/K]	2.2×10^{-6}
M_s	[K]	282
M_f	[K]	287
A_s	[K]	307
A_f	[K]	322

**Fig. 8** Numerical-analytical comparison.

The three described UMAT subroutine has been validated by comparison against analytical models (Ben Jaber and Smaoui, 2006), by considering the NiTiNOL material properties reported in Table 1.

The comparisons, shown in Fig. 8, highlight an excellent agreement between the numerical and analytical results. Finally, Fig. 9 shows a simulation of the shape memory effect computed by the UMAT 3D, considering the effects of the temperature.

According to Fig. 9, the SMA element is initially loaded (1), resulting in a stress-induced phase transition. Then, the stress is removed (2) assuming a constant value of the temperature, resulting in a residual strain. The component is then heated (3), resulting in a temperature-induced phase transition which lead to the removal of the residual strain. The component is finally cooled (4) and returns to its initial condition.

SMA-Based Actuators

SMA-based actuators are devices composed of at least one primary SMA component, in the form of wire or spring. Additionally, the SMA actuator is composed of a restoring element, able to provide a bias force acting against the primary SMA component (Spaggiari *et al.*, 2012). In Fig. 10, different types of actuators are reported and classified according to the restoring element as: one-way, biased, and two-way actuators.

According to Fig. 10, one-way and bias actuators are composed of a single SMA component activated, respectively, by an external load F and by a bias spring, while two-way actuators are composed of two SMA components (primary and secondary). In this article, one-way biased springs actuators have been considered. The behavior of a one-way biased actuator is described in Fig. 11.

According to Fig. 11, unloaded and unconnected SMA and bias springs have been initially considered (Configuration 0). Then, the springs are connected by bridging their free end, applying an overall pre-stretch to both springs (Configuration A). Point A in Fig. 11 is the equilibrium point of the forces exerted by the SMA and the bias springs, which is characterized by a force F_A and a displacement L_C . If heated above the transition temperature, the SMA spring experiences a variation of its elastic modulus (Configuration B), resulting in a new equilibrium point B, characterized by a force F_B and a displacement L_H . The difference ΔF between the equilibrium forces F_B and F_A represents the load exerted by the actuator, while ΔL , which is the difference between the displacements L_C and L_H , represents the stroke of the actuator.

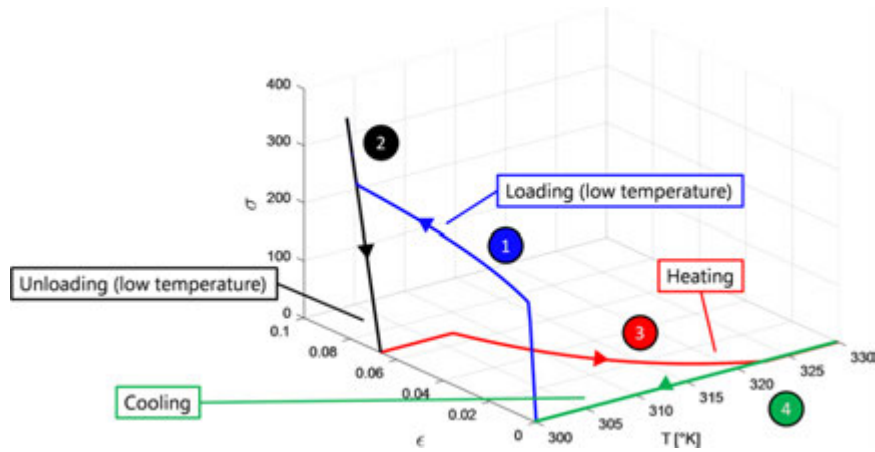


Fig. 9 Shape Memory Effect.

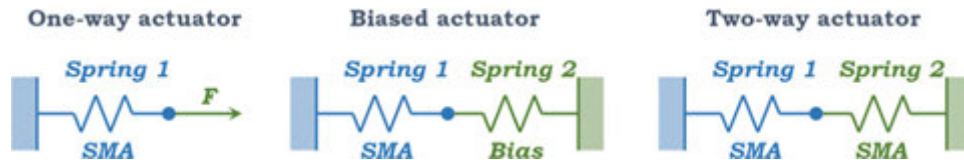


Fig. 10 One-way, biased, and two-way actuators.

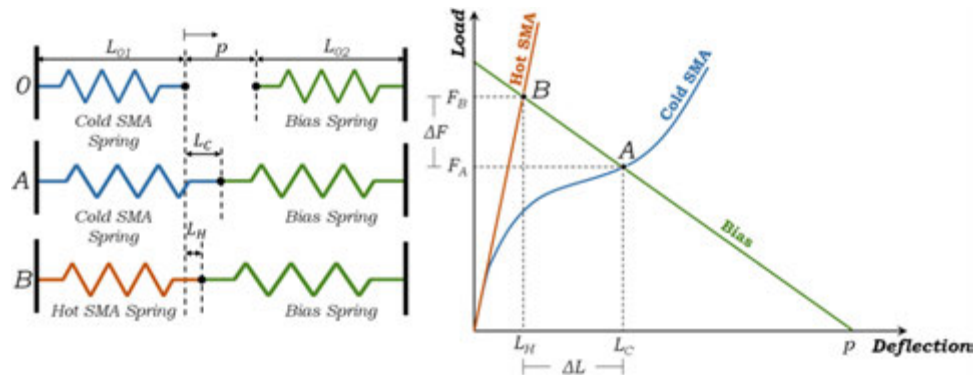


Fig. 11 Two-way SMA actuator behavior. Configuration 0: unconnected SMA and bias springs; Configuration A: equilibrium point between the cold SMA and bias springs; Configuration B: equilibrium point between the hot SMA and bias springs.

Feasibility Study on a Bi-Stable Biased SMA Actuator

A preliminary feasibility study on a bi-stable biased SMA-based actuator is presented. In its initial state, the device starts from an initial stable configuration. Then, the device is actuated by the activation of the SMA spring. Once the SMA spring is deactivated, a second stable configuration (different from the initial one) is reached. A further activation-deactivation of the SMA spring results in the return of the device to the initial stable configuration. Fig. 12 shows the assembled view of the device.

According to Fig. 12, the device is composed of the different parts shown in detail in Fig. 13: a SMA and a Bias spring, a Trust device, a Trust Tube and Guides.

In the first stable configuration, a pre-compression is imposed on the SMA spring, resulting in the equilibrium point A, shown in Fig. 11. Then, the temperature of the SMA component is increased, and a temperature-induced austenite phase transition occurs. Hence, the new equilibrium point B, shown in Fig. 11, is reached, resulting in a force exerted by the SMA spring on the Trust

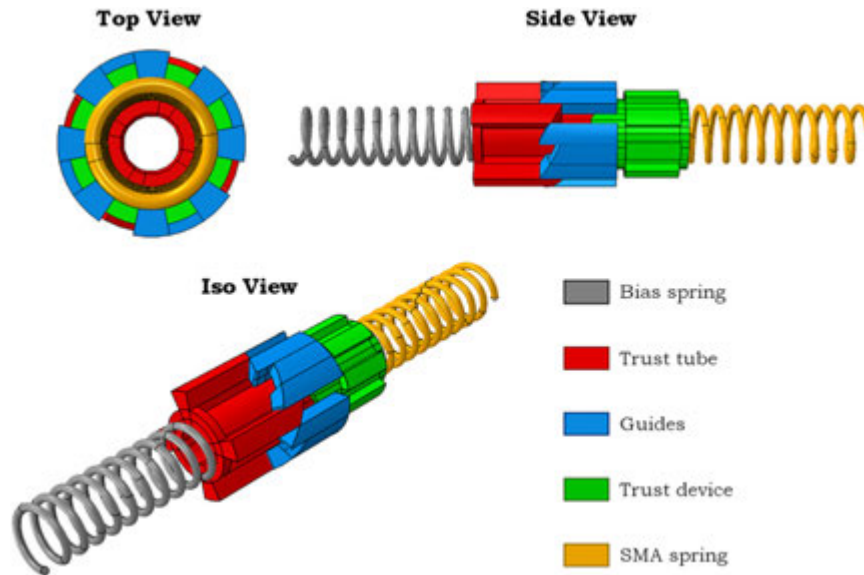


Fig. 12 Bi-stable SMA actuator (Assembled).

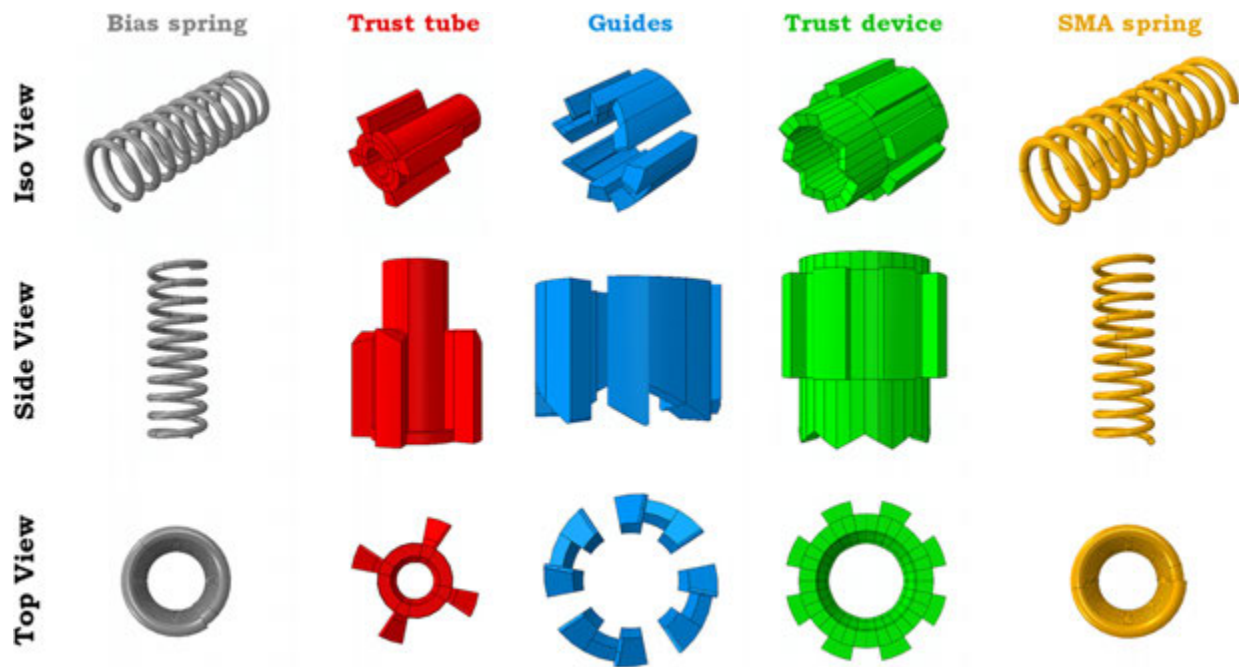


Fig. 13 Device components.

device. Then, the Trust device moves through the guides, pushing the trust tube. The geometry of the device induces a rotation on the Trust tube. The SMA spring is then cooled, and the force applied on the Trust device (and consequently on the trust tube) is reduced. The force exerted by the bias spring overwhelm the one of the SMA spring, pushing the rotated Trust tube toward the guides. Due to the geometry, the rotated trust tube is now blocked by the guides, and a second stable configuration occurs.

Numerical simulations have been used to support the feasibility study. A numerical procedure, which consists in three steps, is introduced to simulate the device behavior.

1. Evaluation of the maximum load needed to actuate the device.

The load exerted by the device, which includes the internal friction and the bias spring forces, is computed by applying a compressive displacement on the Trust device.

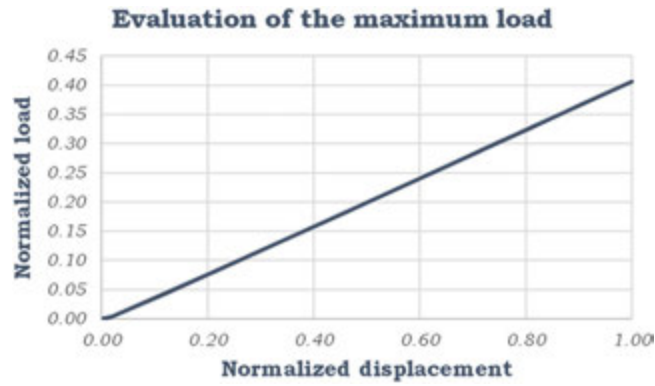


Fig. 14 Maximum load needed to actuate the device.

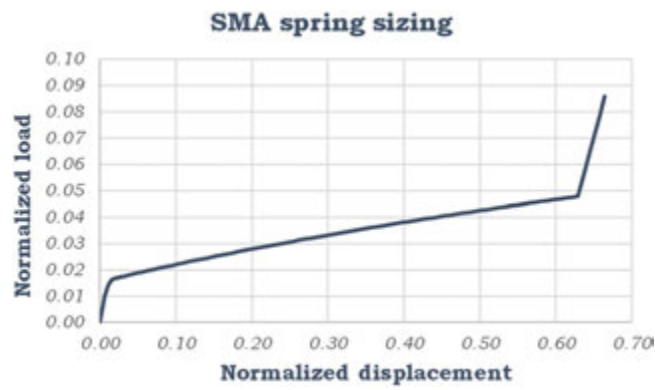


Fig. 15 Load exerted by the pre-compressed SMA spring.

Information on the maximum load needed to actuate the device can be derived from [Fig. 14](#), which reports the load exerted by the device (normalized respect the maximum load exerted by the SMA spring) as a function of the applied displacement (normalized respect the maximum displacement applied to the SMA spring). According to [Fig. 14](#), about 40% of the maximum load exerted by the SMA spring is needed to actuate the device.

2. SMA spring sizing.

The SMA spring is initially compressed, to evaluate the load exerted by the SMA at the beginning of the analysis. In [Fig. 15](#), the load corresponding to the maximum compressive displacement will be equilibrated by the bias spring at the beginning of the analysis. In this way, according to the behavior described in [Fig. 11](#), the device will exert the load during the actuation. Moreover, in [Fig. 15](#) the SMA pseudo-elastic response can be appreciated: the material is initially in its austenite phase; then, the plateau represents the phase transition from the austenite to the final martensite phase.

3. Evaluation of the SMA shape memory effect.

In the third step, the shape memory effect of the SMA is evaluated by increasing the SMA temperature. [Fig. 16](#) reports the load as a function of the temperature, normalized respect to the Austenite finish transformation temperature. According to [Fig. 16](#), the maximum force exerted by the spring correspond to the plateau of the curve, which correspond to at a temperature about 1.35 times the SMA Austenite finish transformation temperature.

To numerically simulate the actuation of the SMA device, several steps of analysis have been considered.

- (1) The SMA spring is precompressed. This step is necessary to obtain an equilibrium between the SMA and bias springs, according to the behavior described in [Fig. 11](#).
- (2) Stabilization of the SMA spring into the model. The device is in its initial stable configuration.
- (3) The SMA spring is heated, to induce a temperature phase transition, resulting in the exertion of a force in the device.
- (4) The SMA spring is cooled, and the device shift to a second stable configuration.
- (5) The SMA spring is heated again, exerting a force on the device.
- (6) The SMA spring is finally cooled, and the device shift from the second stable configuration to the initial stable one (step 2).

[Fig. 17](#) shows the device in its two stable (step 2 and step 4) and intermediate (step 3 and step 5) configurations.

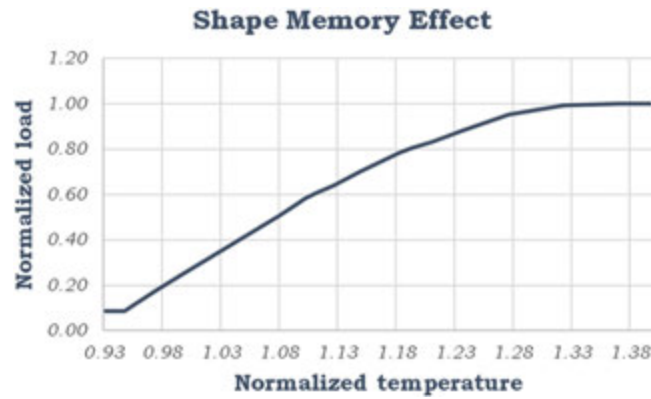


Fig. 16 Load as a function of the Temperature.

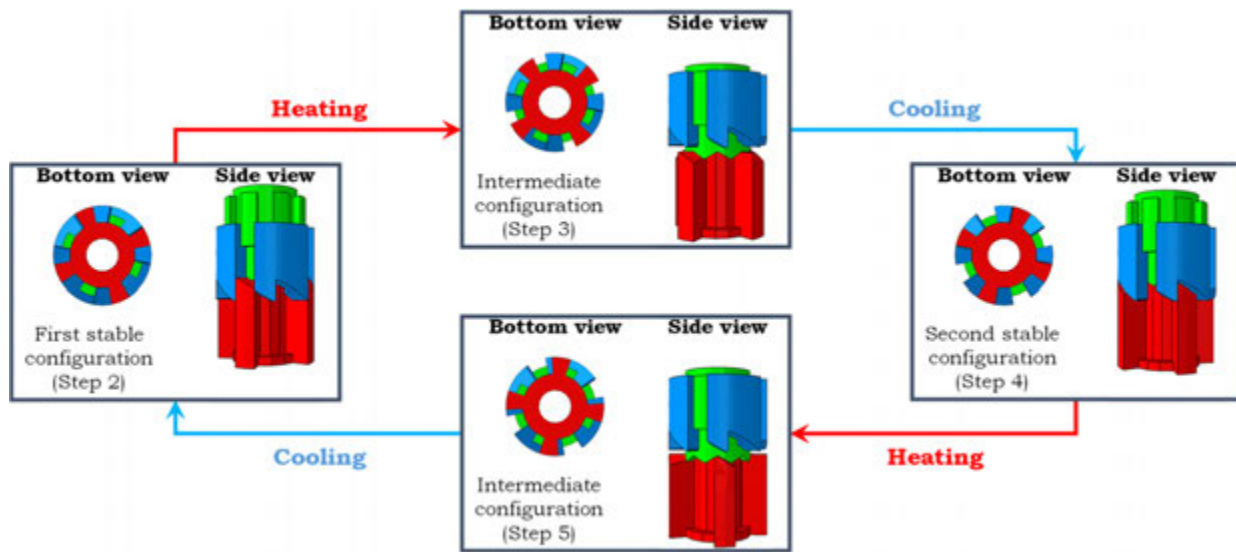


Fig. 17 Device actuation. Step2: first stable configuration; Step 3: intermediate configuration resulting from the SMA spring heating; Step 4: second stable configuration resulting from the SMA spring cooling; Step 5: intermediate configuration resulting from the SMA spring heating; Step 2: first stable configuration resulting from the SMA spring cooling.

Pros and Cons of the Proposed Approach

In this section, the pros and cons of the proposed approach, respect to the state-of-the-art, are briefly listed.

Pros:

- (1) No material model able to describe in detail the SMA mechanical behavior can be found in the most used Finite Element commercial codes. Inversely, the proposed subroutine is able to simulate the SMA mechanical behavior, including the stress-induced Martensite phase transition;
- (2) Bi-stable devices, which are the focus application of this article, are characterized by a reduced thermal and mechanical overstresses and a reduced power consumption with respect to electric current driven standard actuators;
- (3) The proposed device is able to use a single SMA spring to obtain two stable configurations leading to a reduction in the manufacturing and service costs associated to the SMA spring if compared to multiple SMA springs based configurations.

Cons:

- (1) Due to the reduced number of numerical benchmarks considered, the implemented subroutine may experience lack of robustness;
- (2) In order to simulate the SMA mechanical behavior in detail, an extensive characterization campaign on the SMA is needed;

Conclusions

In this work, the behavior of the SMAs has been investigated, including their peculiar shape memory effect and pseudo-elastic behavior, and implemented in the Abaqus finite element code by developing a UMAT subroutine. Different UMATs have been developed, according to the specific problem (1D, 2D, 3D). Validation of the UMATs has been provided, by comparisons with analytical models taken from the literature. Then, a feasibility study on a bi-stable biased SMA-based actuator has been presented. The proposed device is characterized by two stable configurations, in order to reduce the thermal and mechanical overstresses and the power consumption. The numerical simulations have demonstrated the feasibility of the proposed device.

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Thermoresponsive Polymer Nanocomposites

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Introduction

Currently, polymers with stimulus-responsive characteristics play important roles in different fields of applied science. Various polymers with stimulus-responsive properties are also called smart, stimuli-sensitive, intelligent, or environmentally sensitive polymers. These polymers have the ability to respond to different changes present in the surrounding environment (Stuart *et al.*, 2010). The stimuli are classified as physical and chemical stimuli. Physical stimuli correspond to temperature, light, mechanical stress, and magnetic or electrical fields, while chemical stimuli correspond to pH and ionic strength, among others (Gil and Hudson, 2004). Among all the stimuli mentioned above, the effect of temperature on the polymer matrix is one of the most well-studied properties due to the diversity of applications in which the polymer presenting these changes has been employed (Klouda, 2015).

The main characteristic of thermosensitive polymers is the alteration of their structures due to the effects of temperature. These alterations depend on the characteristics of each polymer and the solvent used, leading to phase separation with increasing or decreasing temperature (Weber *et al.*, 2012). Despite the many advantages of thermoresponsive polymers, due to their polymeric nature, these materials still have drawbacks, such as the lack of mechanical robustness, thermal degradation, and poor control of the release of drugs from crosslinked polymers, among others (Berke *et al.*, 2017). Fortunately, many of these drawbacks have been overcome by incorporating nanometer particles into polymers to produce a thermoresponsive polymer nanocomposite. The incorporation of nanomaterials into polymers systems improves or creates a spectrum of novel thermal, mechanical, magnetic, and electrical properties (Aqlil *et al.*, 2017; Cerda-Sumbarda *et al.*, 2020; Diaconu *et al.*, 2019). Nanomaterials, which are defined as materials with at least one length dimension equal to or less than 100 nm, have been classified into (1) zero-dimensional (0D) nanomaterials with a nanoscale size in all three dimensions (spheres), (2) one dimensional (1D) nanomaterials with only one dimension out of the nanoscale range (rods), and (3) two-dimensional (2D) nanomaterials with two dimensions out of the nanoscale range (plates) (Kolahalam *et al.*, 2019). Additionally, there is a fourth classification known as three dimensional (3D), which correspond to materials that are not confined to the nanoscale in any dimension.

The key aspect of a nanocomposite is the substantial increase in the surface to volume ratio as a consequence of the nanoparticle filler, which may improve specific properties compared to larger sized particles loaded in the matrix (Guo *et al.*, 2013). These particular properties place nanomaterials as an intermediate system between molecular entities and their bulk counterpart materials. In general, the effect of nanoparticles (NPs) on the macroscopic properties of a polymer is highly dependent on the nanoparticle–polymer interfacial region, which refers to the area where the polymer chains are perturbed by the presence of the included NPs. The characteristics of this region depend on the type of bond formed between the phases of the material, the confinement of the matrix, and ultimately the potential interference of the NPs on the mobility of the flexible polymer chains (Baxter *et al.*, 2016). Moreover, the interfacial region also depends on the shape of the NPs (or on the particle aspect ratio), thus, the interfacial region is greater when the aspect ratio increases (Winey and Vaia, 2007). Researchers have hypothesized that these interfacial regions would lead to the formation of percolated microstructures by creating interactions between particles and the interface, leading to substantial changes in the mechanical (and electric) properties after the percolation threshold is achieved.

All of these effects are closely related to the important mechanical, optical, magnetic, electrical, and chemical properties of nanomaterials, and thus these types of materials have become the most important structures for applications in areas such as catalysis, biomedicine, nanobioscience, optic-electronic devices, and materials science in the last few decades (Peralta-Videa *et al.*, 2011).

This article aims to describe fundamental information about thermoresponsive polymers and the most recent applications of thermoresponsive polymer nanocomposites. Briefly, the article begins with an overview of the basic concept of thermoresponsive polymers. Next, the incorporation of NPs into the thermoresponsive polymer is reviewed with a special emphasis on “active NPs” consisting of stimuli-sensitive NPs that trigger a subsequent thermal response in the polymer. Finally, the article closes with a review of the most interesting and recent applications of thermoresponsive polymer nanocomposites.

Brief Background of Thermoresponsive Polymers

Thermoresponsive Polymers

Thermoresponsive polymers are materials that exhibit a drastic and discontinuous change in their physical properties with temperature. The most common property studied is solubility, which is temperature-dependent. The thermoresponsive polymer exhibits major changes in conformation both with increasing and decreasing temperature. In this manner, a polymer can present an upper critical solution temperature (UCST) (Schmaljohann, 2006) and a lower critical solution temperature (LCST) (Dimitrov

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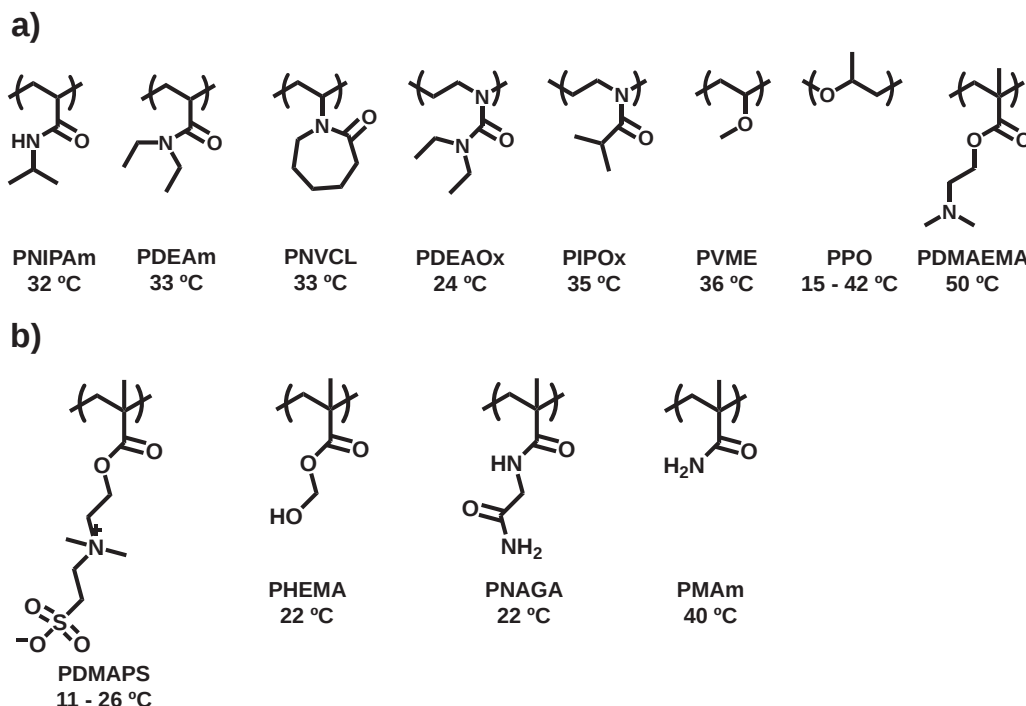


Fig. 1 Chemical structures of some thermosensitive polymers. (a) Polymers with an LCST: poly(*N*-isopropylacrylamide) (PNIPAm), poly(diethylacrylamide) (PDEAm) (Idziak *et al.*, 1999), poly(*N*-vinylcaprolactam) (PNVCL) (Rao *et al.*, 2016), poly(2-diethylamino oxazoline) (PDEAOx) (Sedlacek *et al.*, 2019), poly(2-isopropyl-2-oxazoline) (PIPOx) (de la Rosa, 2014), poly(vinylmethylether) (PVME) (Crespy and Rossi, 2007), poly(propylene glycol) (PPO) (Dai and Tam, 2004), and poly(dimethylaminoethyl methacrylate) (PDMAEMA) (Cho *et al.*, 1997). (b) Polymers with a UCST: poly(*N,N*-dimethyl(methacryloyl)ethyl ammonium propanesulfonate) (PDMAPS) (Niskanen and Tenhu, 2017), poly(hydroxyethyl methacrylate) (PHEMA) (Guo *et al.*, 2016b), poly(*N*-acryloyl glycineamide) (PNAGA) (Seuring *et al.*, 2012), and poly(methacrylamide) (PMAm) (Seuring and Agarwal, 2012).

et al., 2007). The UCST operates when phase separation occurs with decreasing temperature, whereas LCST occurs when increasing the temperature (Maharjan *et al.*, 2008). From a thermodynamic perspective, when the polymer with an LCST comes into contact with water at low temperatures, hydration occurs due to the formation of hydrogen bonds around repetitive units, increasing the solubility of the polymer. However, this hydration implies an entropic penalty due to hydrogen bonds surrounding hydrophobic segments, increasing their contribution with the temperature; hence, at the LCST, water molecules leave to dehydrate the polymer and intermolecular interactions predominate (Tavagnacco *et al.*, 2018). In the case of the UCST behavior, polymers with this type of transition temperature are rarer and the main requirement is strong intramolecular forces (supramolecular interactions, such as electrostatic interactions or hydrogen bonding), which are weakened upon heating, and solvation of the polymer chain occurs through an enthalpy driven solubility phase transition (Zhang and Hoogenboom, 2015). Although these critical temperatures are specific for polymer and solvent, most of the thermoresponsive polymers are studied in aqueous media, and consequently, critical temperatures are associated with the intermolecular forces of hydrogen bonds (see Fig. 1). Thermosensitive polymers have been classified according to certain characteristics with reference to changes in temperature and the nature of their chains as follows: USCT/LCST polymers, polymers based on amphiphilic equilibria, and biopolymers.

One of the most frequently studied thermoresponsive polymers is poly(*N*-isopropylacrylamide) (PNIPAm). This polymer contains amide and propyl residues in the monomeric structure. This polymer exhibits a transition temperature of 32 °C; hence, at low temperatures (<32 °C) the amide groups are highly solvated by water molecules and the polymer is soluble. However, at temperatures greater than 32 °C, the hydrogen bonds weaken and the hydrophobic interactions between the propyl groups are much greater than the hydrophilic interactions, and thus the polymer releases all the water molecules present in its structure and become insoluble (Kumar *et al.*, 2007) (see Fig. 2).

Because thermoresponsiveness mainly depends on the chemical structure of repetitive units and their ability to be solvated or to participate in intramolecular interactions, numerous researchers have incorporated comonomers in the synthesis of new thermoresponsive polymer materials with novel chemical and physical properties. Thermoresponsive copolymers are composed of one or more comonomers, of which at least one should produce a thermoresponsive homopolymer (Liu *et al.*, 2009). The incorporation of comonomers not only modifies the hydrophilic-hydrophobic characteristics and the LCST temperature but also allows other properties to be incorporated into the resulting copolymer, such as increased biodegradability, biocompatibility, pH responsiveness or charge capacity within a thermoresponsive chain (Lanzalaco and Armelin, 2017). Copolymerization also allows the thermoresponsive properties to be transferred to other systems. Various architectures have been reported for thermoresponsive

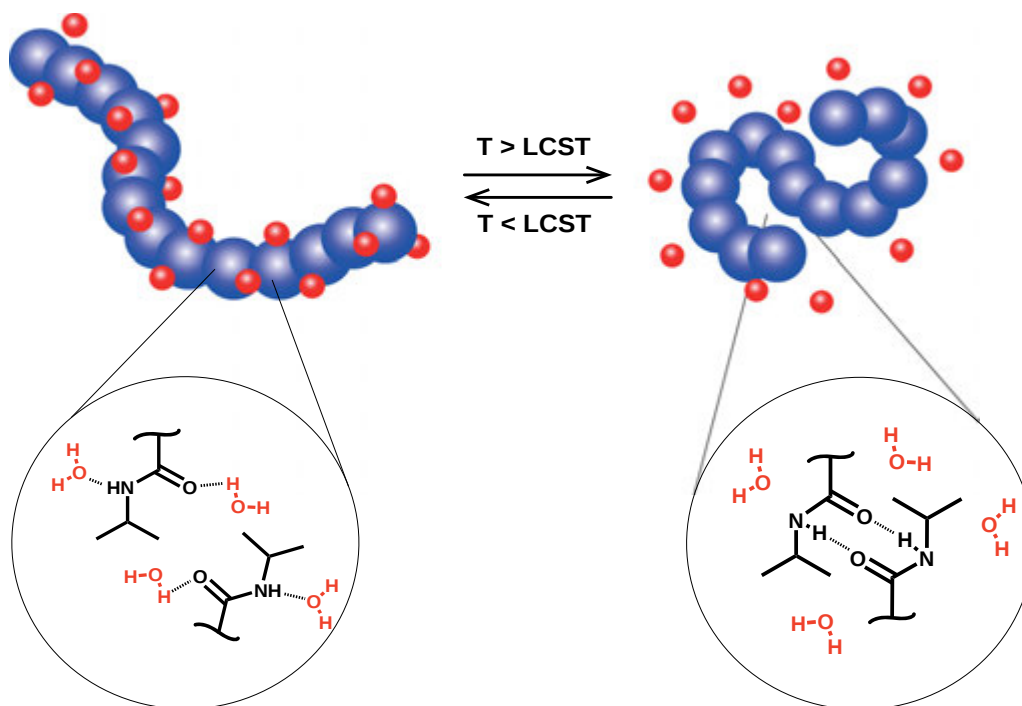


Fig. 2 Conformational change in PNIPAm with temperature.

polymers, including random, graft, block, and comb copolymers (Liu *et al.*, 2009). Block copolymers of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) commercially known as poloxamers (or pluronics) are well known to exhibit temperature-sensitive gelation. The amphiphilicity of PEO-PPO-PEO is attributed to propylene oxide with hydrophobic characteristics and to ethylene oxide with hydrophilic characteristics, and this copolymer exists as a low viscosity solution at room temperature, whereas it forms a gel at body temperature (Ban *et al.*, 2017). Moreover, the thermosensitivity has been tuned by modifying the composition (block lengths), concentration, molecular weight, or mixture of homopolymers (blends) and copolymers (Al Khateb *et al.*, 2016; Hoogenboom and Schlaad, 2017). Similarly, copolymers composed of poly(ethylene glycol) (PEG) and poly(lactic acid-co-glycolic acid) (PLGA) are widely studied in biomedical applications due to their amphiphilic character derived from PEG (hydrophilic) and PLGA (hydrophobic). An example of the use of these types of compounds is the formation of triblock copolymers of PLGA-PEG-PLGA that presents gelling temperatures ranging from 25 to 35°C (Maeda, 2019). On the other hand, based on the hydrophobic characters of poly(propylene oxide), Li *et al.*, synthesized triblock copolymers of PPO and PNIPAm (PNIPAm_x-PPO₃₆-PNIPAm_x) by varying the PNIPAm block with $x = 15, 33, 75$, and 117 , and they were able to modulate the LCST between 25°C and 32°C (Li *et al.*, 2015).

Biopolymers also exhibit temperature-sensitive behaviors (Roy *et al.*, 2013). One of the important features of biopolymers that respond to temperature is that they are able to form physical networks with changes in temperature, and they are attractive because they are often considered non-toxic and biocompatible for different medical applications (Schuetz *et al.*, 2008). Namely, gelatin exhibits a transition temperature at ~32°C (Perera *et al.*, 2019), agarose at 34–38°C (*Gelidium*) and 40–50°C (*Gracilaria*) (Sarah *et al.*, 2019), carrageenan at 30–50°C (Li *et al.*, 2014), and gellan gum between 35 and 42°C (Osmalek *et al.*, 2014). Similar to the synthesis of copolymers, biopolymers can be grafted with a thermosensitive polymer. For example, alginate-g-PNIPAm exhibited a LCST temperature of 37°C and was used to release doxorubicin (DOX) as smart drug delivery system (Liu *et al.*, 2017). Additionally, chitosan-g-PNIPAm displayed an LCST of 32–34°C and was used as a biomimetic cartilage in tissue engineering applications at 32–34°C (Mellati *et al.*, 2017).

Synthesis of Thermoresponsive Polymers

Thermoresponsive polymers are mainly synthesized through a chain growth mechanism via free radical polymerization of a vinyl-based monomer. Although conventional radical polymerization has been conducted, better control of the dispersity and molecular weights has been achieved through controlled radical polymerization. In this manner, thermoresponsive polymers have been successfully synthesized through nitroxide mediated radical polymerization (O'Connor *et al.*, 2012), reversible addition-fragmentation chain transfer (RAFT) radical polymerization (Zhao *et al.*, 2020), and atom transfer radical polymerization (ATRP) (Rahimi and Nasiri, 2020). These polymerization strategies allow greater control of the polymer architecture to obtain block (Ghasemi and Harandi, 2018), dendritic (Kalva and Ambade, 2017), and gradient (Yañez-Macias *et al.*, 2017) polymers. On the other hand, thermoresponsive polymers such as poly(2-oxazolines) are synthesized via (living) cationic ring-opening polymerization, and depending on the

2-substituent, the hydrophilic- hydrophobic balance can be controlled, resulting in a polymer with a tuned LCST (Hoogenboom and Schlaad, 2017). Thermoresponsive polymers have numerous technological applications, but linear soluble polymers do not exhibit the same potential as other polymer materials, such as particles, hydrogels, interpenetrated networks, etc. Polymeric particles with thermosensitive properties have interesting characteristics to be applied in drug delivery systems and disease diagnostics (Wen *et al.*, 2019). Particles from micro to nanometer levels (Saunders *et al.*, 2009) that are porous (Wen *et al.*, 2019), and even nanocomposite thermoresponsive polymer particles have been synthesized (Cors *et al.*, 2017). Hydrogels have been obtained via the physical or chemical crosslinking of their polymer chains. Physical crosslinks are caused by non-covalent interactions, such as Van der Waals forces, electrostatic, dipole-dipole, π - π stacks, and hydrogen bonds, while chemical reticulations have covalent bonds that exhibit greater mechanical stability (Liu *et al.*, 2018); certainly, hydrogels have been synthesized using thermoresponsive polymers (Klouda, 2015; Lyon *et al.*, 2009). Interpenetrated polymer networks are materials formed by mixing two or more polymers, resulting in an interpenetrated structure with a wide variety of properties that depend on the chemical composition of the polymers present in the matrix. These interpenetrated polymers have been classified into simultaneous and sequential polymeric interpenetrated networks according to their chemical preparation (Dragan, 2014), and similar to hydrogels, interpenetrated networks based on thermoresponsive polymers have been synthesized (Guo *et al.*, 2016a; Hamcerencu *et al.*, 2011; Martinez *et al.*, 2018).

Nanoparticles in Thermoresponsive Polymer Nanocomposites

Synthesis of Thermoresponsive Nanocomposites

Different types of nanofillers have been studied to reinforce and/or modulate the properties of polymers. In this article, we will classify these materials into two main groups based on the characteristics of the filler: (1) inert nanofillers and (2) active thermoresponsive nanofillers. In both cases, the presence of the filler alone is sufficient to reinforce the mechanical properties of the polymer. However, the use of active nanofiller may introduce new properties into the nanocomposite and generate a thermoresponse without a direct application of temperature, enabling the possibility to obtain the thermoresponse of nanocomposite using radiation or magnetic field (Satarkar and Hilt, 2008; Zhang *et al.*, 2014b). Four different methods have been well defined with good results to synthesize nanocomposites, as described below.

- (1) Solution mixing method: This approach to nanocomposite synthesis is the simplest (Lu *et al.*, 2014). Here, the nanofiller and the thermoresponsive polymer must be dispersed on a suitable solvent and then mixed to finally remove the solvent in a controlled manner. Some problems associated with a minor dispersion of filler can be resolved by the sonication or functionalization of the polymer.
- (2) *In situ* polymerization: This sequential synthesis method first requires the nanofiller to be dispersed in monomer and crosslinker solutions (Haraguchi *et al.*, 2002). Subsequently, the mixture is polymerized to obtain the hydrogel with entrapped nanofiller.
- (3) *In situ* precipitation/reduction method: This method requires the synthesis of the hydrogel matrix, followed by the incorporation of a solution of the precursor salt of nanofiller, based on their excellent swelling properties (Liang *et al.*, 2007). Then, the salt precursor must be treated with chemical reagents that favor the precipitation or reduction of the nanofiller with the polymer matrix acting as a chemical reactor.
- (4) Grafting-from/Grafting-to method: This method is based on grafting several functional groups onto the surface of nanofiller to transform them into nano-crosslinkers or functionalize them in a polymer chain, which will interact with the filler, leading to the crosslinking reaction (Li *et al.*, 2007). It is considered a promising approach to obtain thermoresponsive ferrogel and thermoresponsive core@shell nanocomposites with homogeneous properties.

Inert Nanofiller

We define an inert nanofiller as a nanomaterial that lacks stimulus-sensitive properties and only functions as a mechanical reinforcement. Nanofillers of this type are silica NPs and clay materials (montmorillonite, laponite, halloysite, etc.) (Djonlagic *et al.*, 2012; Haraguchi *et al.*, 2002; van den Brom *et al.*, 2010). In general, a simple solution to improve the poor mechanical properties is to increase the crosslinking degree; however, the negative consequences on swelling properties, the increase in brittleness, and the possibility of retaining residual crosslinking agent, which is detrimental in materials applied to the medical or food areas, are well known (Ullah *et al.*, 2015). For these applications, inorganic nanofillers have been regarded as an elegant solution to improve mechanical properties and in some cases improve the toughness of the material. Normally, clay nanocomposites are synthesized using *in situ* polymerization with an aqueous dispersion of clay and monomers and further polymerized by radical polymerization (Haraguchi and Takehisa, 2002).

Haraguchi *et al.* evaluated two series of PNIPAm hydrogels with a similar amount of either nanoclay or the chemical crosslinker *N,N'*-methylene-bis-acrylamide, MBAA, (between 1 and 9 mol%) (Haraguchi *et al.*, 2002). Transparency was initially evaluated, and organic crosslinked gels showed an important decrease in transparency at concentrations greater than 3 mol%, while nanocomposites maintained approximately 90% transparency for all nanoclay contents evaluated. An assessment of the mechanical properties revealed the effect of the nanoclay on reinforcing the hydrogel (see Fig. 3). The nanoclay-modified hydrogel

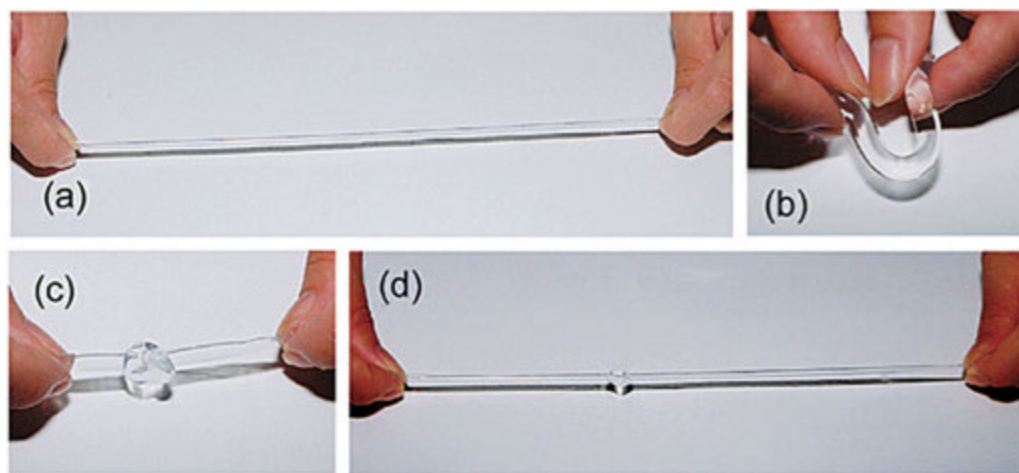


Fig. 3 Effect of laponite nanoclay on the mechanical properties of thermoresponsive PNIPAm hydrogel. Reproduced from Haraguchi, K., Takehisa, T., Fan, S., 2002. Effects of clay content on the properties of nanocomposite hydrogels composed of poly(*N*-isopropylacrylamide) and clay. *Macromolecules* 35 (27), 10162–10171, with permission from Elsevier.

can be elongated by approximately 1000%, while the organic crosslinker hydrogels were very fragile when the tensile modulus was analyzed. Differences observed between the organic crosslinker and nanoclay, as explained by Haraguchi, are attributed to the distribution. The organic crosslinker is expected to distribute randomly throughout the polymer chain, while nanoclays are very well distributed into polymers, particularly at the end of polymer chains, avoiding inhomogeneities in the nanocomposite matrix and acting as a reinforcement over all chains of PNIPAm in a similar manner.

Similarly, *Djonlagic et al.* (2012) reported the preparation of two series of nanoclay-reinforced thermosensitive hydrogels, one based on PNIPAm and the other on semi-interpenetrating networks containing PNIPAm and poly(*N*-vinylpyrrolidone) (PVP). The gels were crosslinked with 1, 3 and 5 wt% laponite. In both cases, an increased concentration of the nanoclay produced an improvement in the mechanical properties of the hydrogel, while elongation deformation increased from 580% to 950% in the swollen state.

Mesoporous silica and silica NPs have also been used as fillers for thermoresponsive polymers due to their beneficial physico-chemical properties, improved stability and possibility of incorporation into the polymer through soft interactions or linkages on the silica surface. Van de Broom *et al.* synthesized films of a nanocomposite based on silica NPs/hydrogel, where the hydrogel is a terpolymer based on NIPAm, methacrylic acid (MAA), and 4-benzoylphenyl methacrylate (MABP), with a monomeric molar ratio in the hydrogel of 0.94, 0.05 and 0.01, respectively, as confirmed from the ^1H NMR spectra in different media. Van de Broom synthesized nanocomposites with a large amount of silica NPs, ranging from 0 to 51 wt% of silica, and evaluated the swelling ratios and critical temperature (T_c) of the film. Silica NPs were obtained using the sol-gel method (35 nm in diameter) and functionalized with benzophenone silane through a reaction with silanol surface groups, where silica NPs functioned as a “supercrosslinker” agent (*van den Brom et al.*, 2010). As expected, the increase in the amount of the crosslinker, namely, silica NPs, produces a decrease in the swelling ratio. At 51 wt% of nanofiller, the swelling ratio decreases up to 1/4 of the capacity with respect to the pure hydrogel. Nevertheless, when T_c is measure in heating mode, it only showed a small but sustained increase with the NPs concentration from 31.2°C to 32.2°C. In another report, *Zúñiga et al.* proposed mesoporous silica with high surface area (higher than 1000 m² g⁻¹) and well-defined internal pores of 6 nm. For this material, mesoporous silica was modified with γ -methacryloxypropyltrimethoxysilane to add a vinyl group that would be further polymerized with PNIPAm to obtain an on-off gate-system because of the thermosensitivity of PNIPAm chains on the silica surface. Then, this system was used as filler in a PNIPAm hydrogel chemically crosslinked with MBA, and the rhodamine B (RhB) release properties were studied (*Zúñiga et al.*, 2017). The nanocomposite functioned as great release material below the LCST temperature and compared with the pure hydrogel, which showed a burst RhB release. This behavior was attributed to the diffusion barriers occurring within the hydrogels, while release decreases at temperatures greater than the LCST because silica pores were blocked due to the collapsed state of the hydrogel.

Another nanomaterial used to reinforce polymers is graphene. Although graphene is considered an active nanomaterial (*vide infra*), the following examples correspond to graphene nanofiller functioning only as a reinforcing agent. Graphene was discovered in 2004 by *Novoselov et al.* (2004), and consists of a 2D one atom thick sheet with a honeycomb shape that assembles based on sp² carbon atoms. Although various synthetic methods have been reported (*Choi et al.*, 2010), the physicochemical approach, which is based on an oxidation process of graphitic carbon in water medium, is the simplest and most convenient method to obtain both graphene oxide (GO) and graphene in large yields (*Kuilla et al.*, 2010). Graphitic carbon is composed of compact layers of graphene, the oxidation of graphite generates a large amount of hydroxyl and epoxy groups and a small amount of carboxylic moieties on the surface, increasing the separation of the layers of GO from 6 to 12 Å and allowing their dispersion in aqueous solution. Additionally, GO possesses a theoretical surface area of 2620 m² g⁻¹; however, synthetic GO has achieved BET surface areas ranging from 400 to 900 m² g⁻¹ (*Park et al.*, 2011). Nevertheless, this surface area is still a larger value than other NPs, suggesting that GO also represents an interesting nanomaterial to be incorporated into thermoresponsive polymers.

Shi *et al.* reported the synthesis of a series of PNIPAm/GO materials using free radical polymerization of NIPAm monomers and MBAA as the crosslinker. GO increased the degree of crosslinking, because the amide groups of NIPAm participate in hydrogen bonding interactions with GO surface groups, and thus GO acts as a reinforcing nanofiller in the PNIPAm hydrogel (Shi *et al.*, 2015); however, GO does not show an effect on the LCST of PNIPAm. Berke *et al.* reported similar results when comparing pure PNIPAm with three nanocomposites of graphene oxide/PNIPAm (GO/PNIPAm), reduced graphene oxide/PNIPAm (RGO/PNIPAm) and reduced graphene oxide/PNIPAm reduced in situ (GO/PNIPAm-R). Berke showed substantial differences between the three nanocomposites. While GO/PNIPAm and GO/PNIPAm-R show an increase in the elastic modulus from 2 to 6 kPa, RGO/PNIPAm did not show differences from pure PNIPAm. The opposite trend was observed for the swelling degree, with decreased swelling for GO/PNIPAm and GO/PNIPAm-R (Berke *et al.*, 2017). The better dispersion of GO in aqueous solution explained these differences, which displayed a better dispersion in the polymer matrix than the RGO nanofiller. All of the examples mentioned in this section correspond to nanocomposites filled with NPs that only function as reinforcers to modify the mechanical performance of final materials; however, active nanofillers have recently attracted the attention of scientific community because these nanomaterials introduce new properties to the nanocomposite, which is described in the next section.

Active Thermoresponsive Nanofiller

We define an active nanofiller as a nanomaterial that possesses stimulus-sensitive properties that improve the response of nanocomposites when incorporated into the polymer matrix. Most of these nanofillers respond to a magnet or electromagnetic radiation, and therefore generate heat that can produce the thermoresponse of the nanocomposite. Examples of this type of nanostructure are carbon-based (graphene, graphene oxide, and carbon nanotubes), magnetic metal oxide NPs (Fe_3O_4), and metal NPs, notably, Au, Ag and Pd NPs (Wei *et al.*, 2007). The next sections will describe some of these active fillers and their effects on the thermoresponse of the nanocomposite.

Carbon-based nanoparticles (CNs)

Graphene, GO, and carbon nanotubes (CNTs) have recognized properties including a superior elastic modulus, unique graphitized planar structure, high conductivity, and large surface area. Furthermore, CNs respond to specific electromagnetic stimuli, generating local heat release (Zhu *et al.*, 2012). The fast optical response in the near-infrared (NIR) range has been discussed by many authors (Chen *et al.*, 2016; Miyako *et al.*, 2008; Seo *et al.*, 2016; Zhang *et al.*, 2011). The wavelength of NIR light ranges from 700 to 1100 nm; it presents negligible absorbance by tissues and deep permeation, and it is easy to operate and can be focused on a specific region. All these properties make CNs interesting fillers for generating thermoresponsive nanocomposites with a change in properties in the presence of various external stimuli and promising applications as therapeutic drug transport systems (Cirillo *et al.*, 2014). For example, Lo *et al.* modified GO through the esterification of surface carboxylic acid group with glycidyl methacrylate, which was then photopolymerized together with NIPAm, and evaluated the response of nanocomposite in DMSO to NIR irradiation. They confirmed a fast and substantial increase in temperature from room temperature to 41°C within two minutes of irradiation, resulting in an estimated heat release of 63.21 J compared with a negligible temperature increase of pure DMSO under NIR radiation (see Fig. 4; Lo *et al.*, 2011).

On the other hand, CNTs consist of 1D nanocylindrical structure based on single (SWCNTs) or multi-walled (MWCNTs) with a hexagonal arrangement of carbon-carbon bonds (Tserpes and Papanikos, 2005). A simple consideration to understand the CNT structure is to visualize structures formed by rolling graphene sheets. In general, researchers report different values for the physical properties of CNTs, but they all confirm that CNTs possess unique mechanical, electrical and thermal properties (see Table 1; Ma *et al.*, 2010).

Nevertheless, similar to graphene sheets, the molecular assembly is based on sp^2 carbon atoms associated with strong π - π interactions between single tubes, generating aggregation and a water-insoluble character. Zhang *et al.* report the synthesis, thermal characterization, and thermoresponse to NIR light of UV polymerized SWCNTs/PNIPAm nanocomposites with a CNT concentration ranging from 0.25 to 1 mg mL^{-1} and MBAA as the crosslinker (Zhang *et al.*, 2011). Due to the similarity with graphene and GO, the incorporation of CNT into the PNIPAm polymer does not significantly alter the LCST. Moreover, the response of CNTs/PNIPAm to the NIR laser was monitored by imaging with a charge-coupled device camera (CCD camera) (see Fig. 5). Interestingly, nanocomposites showed a black spot upon laser exposure compared with pure PNIPAm that does not show this effect, confirming the heat release-like response to NIR irradiation conferred by the CNT filler (Zhang *et al.*, 2011). Similarly, Wu *et al.* analyzed the effect of CNTs on the LCST of PNIPAm, but in this case, CNTs were modified with a pendant benzyl sulfonate group and hydrogel matrix by co-polymerizing N-isopropylacrylamide (NIPAAm), MBAA and (3-acrylamidopropyl)trimethylammonium chloride to obtain a PNIPAm hydrogel with trimethylammonium pendant group and larger interconnected pores. An increase of 5°C in the LCST was observed and attributed to the strong electrostatic interaction between pendant group (Wu *et al.*, 2013).

A simple conclusion of the incorporation of nanocarbon materials into hydrogels is that typical Van der Waals type interactions do not modify the LCST, but when the interactions between the filler and polymer are reinforced, the LCST increases substantially. A similar effect has been reported for chemically crosslinked hydrogels, where polymer chains are interconnected by strong bonds. In the study by Žugić *et al.*, an increase in the LCST was observed with an increasing amount of crosslinking agent (Žugić *et al.*, 2009). In another study,

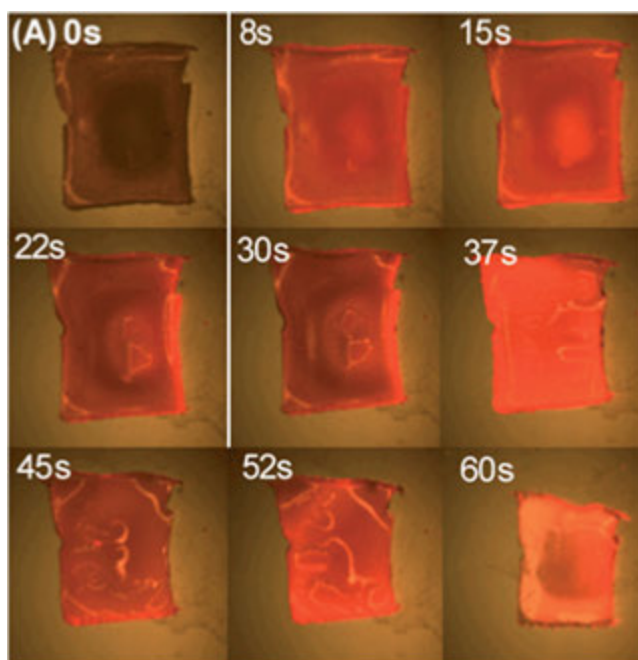


Fig. 4 Dynamic change in GO/PNIPAm in response to a NIR laser cycle. Adapted from Lo, C.-W., Zhu, D., Jiang, H., 2011. An infrared-light responsive graphene-oxide incorporated poly(N-isopropylacrylamide) hydrogel nanocomposite. *Soft Matter* 7 (12), 5604–5609, with permission from the Royal Society of Chemistry.

Table 1 CNT properties

Characteristic	SWCNTs	MWCNTs
Interlayer separation (nm)	–	~ 0.34
Outer diameter (nm)	0.6 – 2.4	2.5 – 100
Elastic modulus (TPa)	1–3.6	~ 0.3 – 2.4
Strength (GPa)	50–500	10–60
Electrical conductivity (S cm^{-1})	$10^2 - 10^6$	$10^3 - 10^5$
Thermal stability (K)	> 600	> 600

Jaiswal *et al.* discussed the possibility of modifying the LCST of nanocomposite polymers based on PNIPAm using nanofillers with hydrophilic groups on their surface (Jaiswal *et al.*, 2014).

Gold nanoparticles (Au NPs)

The use of metal NPs as reinforcement has been widely studied to enhance the properties of polymers (Xu *et al.*, 2003). Au NPs have received particular attention due to their electrical conductivity, optical properties, strong surface plasma resonance (SPR) (Janovák and Dékány, 2010), and their diverse synthetic methods (Skrabalak *et al.*, 2008). Gold NPs are particularly interesting for their applications in areas such as photodynamic and photothermal therapy. In these applications, due to their surface plasmon resonance (SPR) effect, collective conversion oscillation of electrons on the surface causes SPR at specific frequencies of light and results in the strong extinction of electrons, converting light into heat and generating the hyperthermia phenomenon. This effect mainly depends on variables such as the size, shape, surface, and state of aggregation of the NPs (Nehl and Hafner, 2008). Furthermore, the absorbed energy is converted to heat based on electron–electron and electron–phonon interactions (Kah *et al.*, 2015), which are useful to induce a conformational change in thermoresponsive polymer. Kurdtabar *et al.* reported the synthesis of a hydrogel composed of PNIPAm-carboxymethylcellulose (CMC) around Au nanorods (GNR) (Kurdtabar *et al.*, 2019). The obtained GNR/PNIPAM-g-CMC hydrogel showed a greater swelling capacity at different times and temperatures than the PNIPAM-g-CMC hydrogel. Kurdtabar associated this increase with the presence of nanorods, which caused repulsion between polymer chains. In addition, no modification of the phase transition temperature was reported. The UV-vis spectroscopy characterization of composite showed both plasmon absorptions (transverse surface and longitudinal plasmon resonance bands) of gold nanorods at 510 and 750 nm. The latter band suggests the possibility of stimulating the composite with a NIR laser and generate the collapse of the polymer due to heat released by the nanorod component.

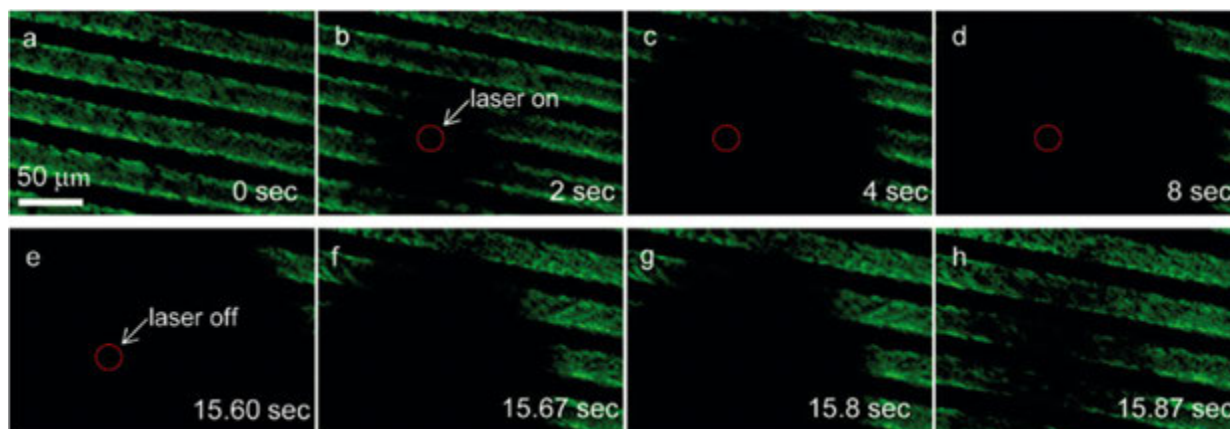


Fig. 5 CNTs/PNIPAm response to the NIR laser. Reprinted with permission from Zhang, X., Pint, C.L., Lee, M.H., *et al.*, 2011. Optically- and thermally-responsive programmable materials based on carbon nanotube-hydrogel polymer composites. *Nano Letters* 11 (8), 3239–3244, Copyright 2011, American Chemical Society.

Li *et al.* synthesized decorated Au NPs by grafting an initiator with a sulfur, disulfide or thiol group onto Au NPs to obtain a well-defined core-shell nanocomposite structure using an Au core covered by PNIPAm chains crosslinked with MBAA (Li *et al.*, 2007). Transmission electronic microscopy (TEM) revealed the phase transition with a noticeable difference in the size of the nanocomposite when the temperature increased above the LCST, with 160 nm at 25°C and 112 nm at 38°C. Other interesting applications of Au NPs as nanofillers in thermoresponsive polymer nanocomposites will be described in the applications section.

Magnetic iron oxide nanoparticles

Among the diverse magnetic NPs, iron (II) oxide (Fe_2O_3) and iron (III) oxide (Fe_3O_4 , ferrite) have unique magnetic size-dependent properties (Laurent *et al.*, 2008), such as the ability to be affected by alternating magnetic fields (AMF) to release heat. The application of a magnetic field to magnetic nanoparticles (MNPs) is addressed using four models: (1) eddy currents, (2) hysteresis loss, (3) Brownian relaxation, and (4) Néel relaxation. However, the explanation of the increase in the temperature of magnetic materials cannot be explained by any of the four independent models.

Eddy currents are related to a very fast change in magnetic flux, but they are associated with the bulk state of matter and therefore do not apply to MNPs dispersed on materials, as in nanocomposites; meanwhile, the hysteresis loss effect decreases as the MNP size decreases due to volume and coercivity (Deutsch and Evans, 2014).

On the other hand, relaxation losses that are induced in a magnetization process can be explained by different relaxation processes, and the two most typical mechanisms reported to understand the temperature change of MNPs with a size less than 20 nm are the Brownian and Néel relaxation mechanisms associated with a delay in the relaxation of the magnetic moment (see Fig. 6). In the first mechanism, heat is produced by rotating the magnetic moment in a static matter state, while in Néel relaxation, the magnetic moment is fixed and the particle rotates, which generates an increase in temperature (Suto *et al.*, 2009).

The large surface area, biocompatibility, and variety of synthetic methods for MNPs to obtain a monodispersed size of the material has allowed them to become important materials that have been applied in medicine as sensors, biomarkers, steerable drug carriers, and cancer treatment systems (Laurent *et al.*, 2008). However, sintering or agglomeration is an inherent drawback related to magnetic properties in the nanoscale dimension. Therefore, an elegant solution is to stabilize the magnetic particles with nanocomposite materials, and thermoresponsive hydrogel matrices are an excellent option to maintain the biocompatibility of materials; this type of nanocomposite is specifically called “thermoresponsive ferrogel” (Hyk and Kitka, 2018). Furthermore, magnetic particles provide the mechanical support to the hydrogel matrix as a synergistic effect and enabling AFM to be used to induce the thermal response of the hydrogel matrix. Jaiswal *et al.* reported composites based on Fe_3O_4 MNPs encapsulated in the PNIPAm hydrogel matrix synthesized using the in situ polymerization approach. In addition, the LCST of the composite has been modulated by modifying the surface of MNPs. PEG-dicarboxylate and PSS hydrate-octakis(tetramethylammonium) were used to modify MNPs, generating an increase of approximately 10°C in the LCST, which was associated with the high hydrophilicity provided by PEG and tetramethylammonium (Jaiswal *et al.*, 2014). DOX was used to evaluate the response of the nanocomposite charged at the radiofrequency field (RF). An important difference between irradiated a non-irradiated DOX-NC system was reported. While the non-irradiated system was only able to release 18% of DOX after 48 h, the system irradiated for 1 h with RF showed twice the release after being measured after 48 h. Jaiswal associated this noticeable difference in the percentage of DOX release to MNP vibration and local heat release produced by the RF application (Jaiswal *et al.*, 2014).

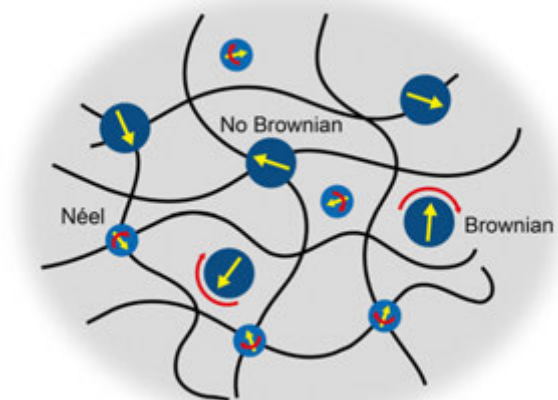


Fig. 6 Néel and Brownian relaxation models. Reproduced from Van Berkum, S., Dee, T.J., Philipse, P.A., Ern , H.B., 2013. Frequency-dependent magnetic susceptibility of magnetite and cobalt ferrite nanoparticles embedded in PAA hydrogel. *International Journal of Molecular Sciences* 14 (5), 10162–10177.

Applications of Thermoresponsive Polymer Nanocomposites

In recent years, the ability of thermoresponsive polymers to respond to temperature changes has been coupled with the different properties provided by nanocomposites (structural reinforcement and response to a magnetic field, light, energy, and ultrasound), producing a synergistic effect on the obtained nanocomposite materials. These thermoresponsive polymer nanocomposites have been shown to have multiple biomedical, analytical, catalytic, new material development, and other applications. Some of the most recent and relevant applications of thermoresponsive polymers nanocomposites in these areas are described below.

Biomedical Applications

Thermoresponsive polymer nanocomposites are attractive materials for biomedical applications, due to their structural similarity to many tissues, architectural versatility, and the ability to deliver drugs in a minimally invasive manner. Drug delivery systems and tissue engineering are among the biomedical applications in which these materials exert the greatest effects.

Drug delivery systems

Most likely, one of the areas where more research has been conducted is in drug delivery using thermoresponsive polymer nanocomposites as the drug carrier. In many of the studies reported to date, the properties provided by NPs are coupled with the properties supplied by the polymer to achieve better performance in both the delivery and the release rate of the drug (Gao *et al.*, 2020a; Lu *et al.*, 2014). An excellent example of this type of coupling focused on controlling the drug release is described in the study by Zhang *et al.* (2014b), where gold nanorods were encapsulated in polymers to couple the photothermal properties of gold nanorods and the thermo- and pH-responsive properties of polymers poly(*N*-isopropylacrylamide-*co*-acrylic acid) in a single nanocomposite. The activation mechanism was transformed from heat to an NIR laser, which is able to be more easily controlled. The material was used for the controlled release of DOX, a clinical cancer drug, which binds to the nanocomposite through electrostatic interactions. With this material, anti-cancer drugs were delivered through a laser activation mechanism with easy control of the area, time and dose. This NIR laser-induced cancer-directed thermochemotherapy represents a new anti-cancer strategy that is easy to control and highly effective using the combined action of thermoresponsive polymers and NPs.

Multiple studies have reported greater control of drug release by incorporating NPs into thermoresponsive polymers. An interesting study focused on the controlled release of drugs in which the synthesis of a novel intelligent thermoresponsive-magnetic molecularly imprinted polymer (MIP) nanocomposite based on PNIPAm and Fe₃O₄ NPs designed for the controlled release of curcumin was reported by Sedghi *et al.* (2018). In this study, MIPs with the capacity for the molecular recognition of curcumin were obtained. Due to the thermoresponsive properties of the polymer, the controlled release of the drug was achieved. Additionally, the presence of MNPs helped facilitate the extraction and transport processes.

Another method to control drug release was reported by Brunella *et al.* (2016). In this study, PNIPAm and mesoporous silica NPs (MSNP) were used to transport and release ibuprofen. The MSNP transported the ibuprofen, while the PNIPAm regulated the release of the drug from the pores of the MSN in response to changes in the temperature of the solution.

Thermoresponsive polymer nanocomposites are at the forefront of research in drug delivery systems. In general, many researchers have reported that the incorporation of NPs into thermoresponsive polymers has generated greater control of both the material and the release of drugs (Gao *et al.*, 2020a; Salimi *et al.*, 2018; Yue *et al.*, 2019).

Tissue engineering

Tissue engineering aims to replace tissues or organs that are damaged or diseased and allow the body to regenerate or develop a new, functional tissue. It is usually achieved through a three-dimensional matrix or scaffold that contains bioactive molecules, living cells, and growth/differentiation factors (Nagahama *et al.*, 2018). These systems must support the cellular union, proliferation, migration, and subsequent implantation of this scaffold at the site of the damaged tissue within the body (Ashraf *et al.*, 2016). The scaffold material should be biocompatible, biodegradable, porous, highly resistant, and easy for the clinician to process (Prabaharan and Mano, 2006). The use of thermoresponsive polymers such as PNIPAm in tissue engineering has attracted the attention of the scientific community because its LCST is approximately 32°C. This feature allows cells to bind to the PNIPAm surface to proliferate at temperatures greater than the LCST, and the cells detach from the PNIPAm surface as a cell sheet after the temperature reaches a value below the LCST. Typically, when developing tissue engineering procedures, rapid detachment of this cell sheet is desired. PNIPAm has a limited biocompatibility and biodegradability; however, the incorporation of nanofillers has been proven to improve the biocompatibility, biodegradability, mechanical properties, and the magnetic or electrical conduction (Xu *et al.*, 2020).

Wang *et al.* described the synthesis of a temperature-sensitive nanocomposite hydrogel obtained from the polymerization of PNIPAm in a suspension of aqueous laponite hectorite containing the polysaccharide alginate (Wang *et al.*, 2011). The obtained material was thermally sensitive and possessed excellent mechanical properties. The decrease in temperature produced a rapid detachment of the cell sheet from the gel surface (see Fig. 7). The separated cell sheet was seeded and proliferated again, showing good cell viability, indicating that the obtained material has promising applications in tissue engineering. Similarly, the synthesis of a nanocomposite hydrogel based on PNIPAm, polyethylene glycol dimethacrylate and GO nanosheets was reported (Xia *et al.*, 2019). The incorporation of the nanofiller was shown to improve the biocompatibility of the scaffold. Furthermore, the cells were able to bind and proliferate, and intact cell sheets were harvested from the hydrogels simply by decreasing the temperature.

Injectable thermoresponsive polymers have received increasing attention in this area due to the capacity of form gels in situ at the diseased sites and therefore avoid invasive painful surgical procedures (Nelson *et al.*, 2011). This characteristic is attributed to the liquid state of thermoresponsive polymers at room temperature, but they solidify when entering the body (37°C), generating a 3D system ideal for cell growth and the easy incorporation of growth factors. In the study by Baei *et al.* thermoresponsive polymer nanocomposites were used as an injectable polymer that resembled the electromechanical properties of the myocardium (Baei *et al.*, 2016). The material was synthesized using chitosan and gold NPs, generating a heat-sensitive conductive hydrogel (due to the incorporation of highly conductive NPs). The scaffolds obtained supported the viability, metabolism, migration, and proliferation of mesenchymal stem cells and the development of uniform cell constructs. Furthermore, the scaffold improved the properties of myocardial constructs, serving an excellent alternative for the regeneration of other electroactive tissues. Overall, thermoresponsive polymer nanocomposites are very promising materials for applications in tissue engineering since they allow researchers to obtain scaffolds that imitate the structures and properties of the extracellular matrix very well.

Analytical Applications

Sensors

In recent years, researchers have expressed substantial interest in the development of sensors and biosensors based on thermoresponsive polymers nanocomposites (Abraham *et al.*, 2018). These types of materials have the ability to undergo conformational changes and generate responses that can be analyzed. They also generate on/off states for the sensors as a function of temperature. An example of this type of application is shown in the study conducted by Mutharani *et al.* (2020), in which the construction of an electrochemical detection film for the herbicide acetonitrile was reported. The sensor was composed of PNIPAm, poly(aniline) (PANI), and Cu NPs and was built on a glassy carbon electrode (GCE). The fabricated sensor exhibited reversible “on/off” electrochemical performance as a function of the temperature of the buffer solution, which was attributed to the presence of PNIPAm in the film (see Fig. 8). The resulting material also achieved good recovery in lake water samples for the determination of the analyzed herbicide. Similarly, Chen *et al.* (2018a) reported the synthesis of a sensor for glucose detection. This study shows the synthesis of a thermoresponsive polymer nanocomposite composed of PNIPAm and CuO NPs using ultrasonic polymerization under N₂ aeration. The obtained sensor presented high sensitivity to glucose and on/off states, depending on the temperature in the range of 25–45°C.

Regarding biosensors obtained using thermoresponsive polymers nanocomposites, Gong *et al.* (2014), reported the synthesis of poly(*N*-isopropylacrylamide)-*co*-poly(methyl methacrylate) nanofibres manufactured by electrospinning, which were mixed with titanium dioxide (TiO₂) NPs grafted with PNIPAm. The resulting nanocomposite was used to detect daunorubicin. Additionally, tests were conducted by adding DNA to improve the biorecognition of daunorubicin. At temperatures above the LCST, a self-assembly process occurred between the nanocomposites, daunorubicin, and the DNA. The self-assembled composite not only displayed an improvement in the detection sensitivity but also efficiently facilitated the binding of daunorubicin to DNA. Additionally, because self-assembly varies with temperature, the response of daunorubicin is expected to be controlled by temperature. The biosensor developed in this study exhibits excellent sensitivity and has potential applications in the detection of drugs for target diseases.

Thermoresponsive polymer nanocomposites are an excellent alternative for the development of sensors and biosensors, since they enable controlled detection and generate “on/off” states through changes in temperature.

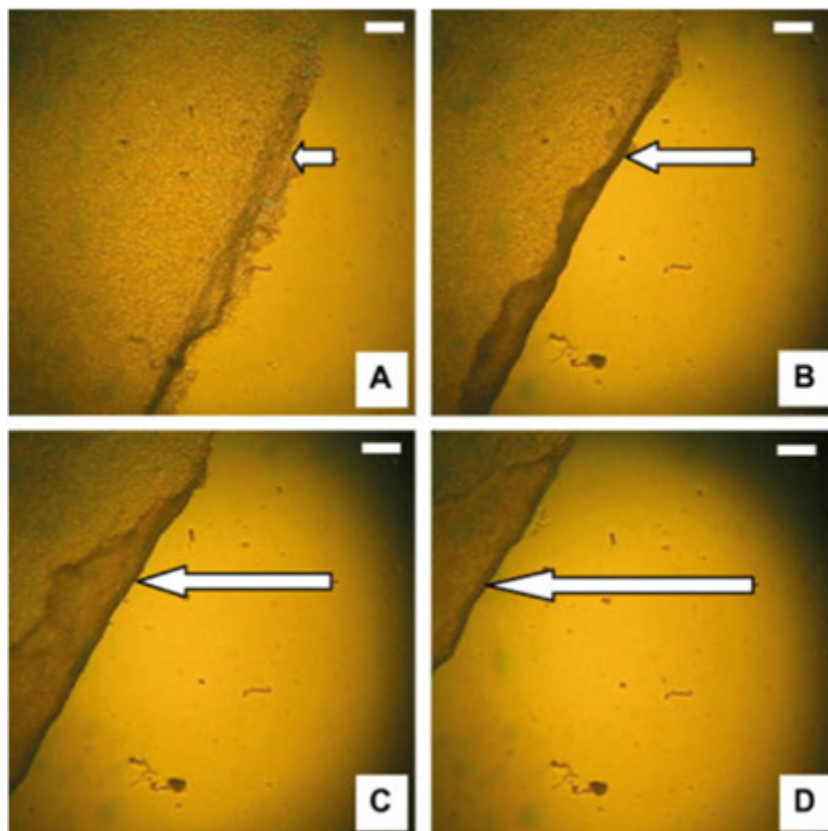


Fig. 7 Detachment of a fibroblast sheet from the gel induced by decreasing the temperature to 10–20°C. A micrograph captured 5 min after decreasing the temperature (A) and micrographs captured every 30 s (B–D) are shown. Scale bar: 100 μm . Reproduced from Wang, T., Liu, D., Lian, C., *et al.*, 2011 Rapid cell sheet detachment from alginate semi-interpenetrating nanocomposite hydrogels of PNIPAm and hectorite clay. *Reactive and Functional Polymers* 71 (4), 447–454, with the permission of Elsevier.

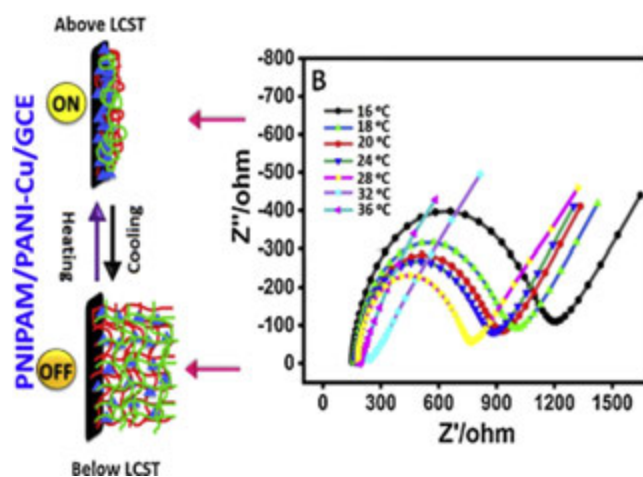


Fig. 8 Electrochemical impedance spectra of the PNIPAM/PANI-Cu/GCE in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe containing 0.5 M KCl at various temperatures (16–36°C). Adapted from Mutharani, B., Ranganathan, P., Chen, S.-M., 2020. Stimuli-enabled reversible switched acclonifen electrochemical sensor based on smart PNIPAM/PANI-Cu hybrid conducting microgel. *Sensors and Actuators B: Chemical* 304, 127232, with the permission of Elsevier.

Catalytic applications

The use of metal NPs in catalysis is widely known. However, one of the main limitations of NPs is their limited colloidal stability, which leads to the formation of aggregates and consequently to a reduction in the catalytic activity (Satapathy *et al.*, 2017). An alternative to

improve the stability of NPs is to use thermoresponsive polymeric supports. The use of stabilized NPs in thermoresponsive polymers allows the creation of thermo-sensitive catalytic systems where the catalytic activity is adjusted by the temperature. An example of this type of synergy between the catalyst and the support is reported by Wang *et al.* (2017). The authors report the synthesis of the thermoresponsive polymer poly(*N*-isopropylacrylamide-*co*-episulfide) and reduced GO @Fe₃O₄@Au magnetic nanocomposites. The obtained material exhibited temperature-dependent catalysis of nitrophenol reduction.

A similar behavior was reported in the study by Li *et al.* (2018), where an Ag-Au bimetal-embedded poly(*N*-isopropylacrylamide-*co*-3-methacryloxypropyltrimethoxysilane) was used for the catalytic reduction of 4-nitrophenol. The catalytic activity of this system was controlled by temperature. When the temperature was below the LCST (25–30°C), the PNIPAm was in an extended state and therefore the catalytic activity increased as the temperature increased. At temperatures near the LCST (30–32°C), the contraction of the PNIPAm chain blocked the contact between the reagent and the bimetal Ag-Au catalyst, decreasing the catalytic activity. Finally, at temperatures greater than the LCST (32–40°C), the catalytic activity was much higher, mainly due to a lower activation energy.

Based on these results, thermoresponsive polymer nanocomposites are an excellent alternative as a heterogeneous catalyst with the ability to generate NP stabilization and catalytic activity controlled by temperature.

New Material Development Applications

Self-healing materials

Self-healing materials represent the forefront of the most recent developments taking advantage of the synergy between chemistry and engineering. These types of bioinspired materials have the ability to repair themselves. When the polymers are in the molten state, they present a higher interfacial diffusion and chain mobility. This feature has been used by different researchers to generate new materials with self-healing properties from thermoresponsive polymers (Yang and Urban, 2013). Cheng *et al.* (2019), reported the synthesis of a new material consisting of two layers of hydrogels (PNIPAm and poly(*N,N*-dimethylacrylamide)) that incorporated GO NPs and clays. The resulting material presented very good mechanical properties and a fast self-healing capacity (60 s) driven by NIR (see Fig. 9(a)). Furthermore, by combining both hydrogels, the obtained material functioned as a “hinge”. This material underwent a rapid deformation in the presence of NIR irradiation and returned to its original form in the absence of irradiation, representing a repeatable process (see Fig. 9(b)). These types of materials have potential applications in soft actuation, flow control and biomimetic devices.

The self-healing capacity has also been integrated with other properties, such as electrical conductivity and elastic properties, to generate new materials with potential applications in the field of biomedicine. Deng *et al.* (2019) reported the synthesis of new self-healing conductive nanocomposites based on a nanoclay (laponite), MWCNTs and PNIPAm. The materials rapidly responded to both light and NIR, due to the high efficiency of CNTs to transform the energy absorbed in the form of NIR to heat and the ability of PNIPAm to generate a volume change as a response to temperature changes. The laponite nanoclay served as a physical crosslinker, improving the mechanical, adhesive and self-healing properties of the hydrogel.

Another excellent application of self-healing polymers is their use as injectable hydrogels for tumor control. Due to their self-healing capacity, after an intratumour injection, the hydrogels reunite after suffering damage and integrate into an entire hydrogel. These characteristics have been used efficiently in the study by Wang *et al.* (2020). The authors describe the synthesis of a self-healing, thermoresponsive hydrogel composed of poly(2-(dimethylamino) ethyl methacrylate-*co*-2-hydroxyethyl methacrylate) modified with

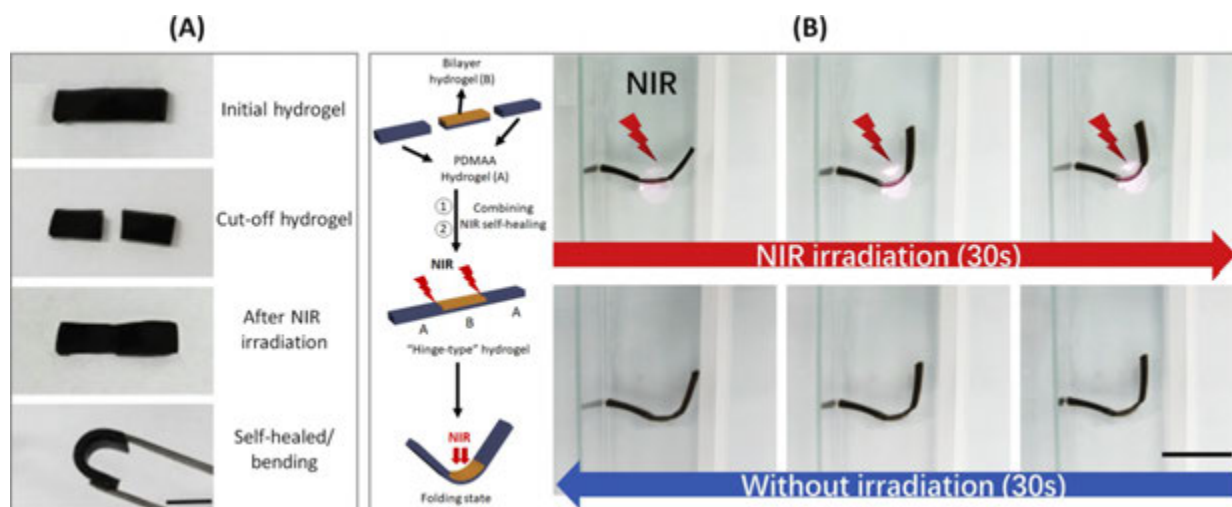


Fig. 9 Self-healing thermoresponsive polymer nanocomposites of PNIPAm and poly(*N,N*-dimethylacrylamide) and GO nanoparticles. (A) Self-healing capacity and (B) “hinge” behavior. Adapted from Cheng, Y., Ren, K., Huang, C., Wei, J., 2019. Self-healing graphene oxide-based nanocomposite hydrogels serve as near-infrared light-driven valves. *Sensors and Actuators B: Chemical* 298, 126908, with the permission of Elsevier.

tert-butyl acetoacetate (*t*-BAA). After adding polydopamine nanoparticles (PDANPs), the hydrogel was loaded with the anticancer drug DOX to be injected as an intratumour drug. After the injection and irradiation with NIR, the temperature of the hydrogel increased due to the photothermal effect of PDANPs that induced local hyperthermia. The increase in temperature generated a hydrophilicity-hydrophobicity transition of the hydrogel, and consequently, DOX molecules were expelled from the hydrogel at temperatures greater than its LCST. The tumor cells suffered internal stress due to the shrunken hydrogel. The injectable polymer was not only an excellent alternative to highly efficient thermochemotherapy but also improved drug utilization for the prevention of side effects.

This section has described the great versatility of self-healing thermoresponsive polymer nanocomposites for use in various applications, both in biomedicine and in the development of new materials.

Shape memory materials

Shape memory polymers are a novel class of programmable materials with the ability to memorize two or more original shapes and recover them after exposure to an external stimulus (heat, light, electricity, magnetic field, pH or humidity). The addition of nanofillers to thermoresponsive shape-memory polymers attracted the attention of the scientific community, as it allowed the design of new materials with custom properties and characteristics (Cudjoe *et al.*, 2017). The resulting materials presented improved mechanical, thermal and electrical properties with respect to their counterparts without nanocomposites, confirming the synergy generated between the polymers and nanofiller used in this type of material (Cudjoe *et al.*, 2017). Extensive research is still ongoing with thermoresponsive shape-memory polymer nanocomposites and their applications, which include aerospace and biomedical devices, textiles, sensors, optics, and adhesives (Marotta *et al.*, 2018; Yenpech *et al.*, 2019). Gopinath *et al.* (2020), reported the synthesis of a new material composed of polycaprolactone, polystyrene-*block*-polybutadiene-*block*-polystyrene, and carbon nanofibres. The obtained material presented thermosensitive memory properties. Furthermore, the mechanical and conductivity properties were improved following the incorporation of nanofillers.

In another study, Yenpech *et al.* (2019) proposed an in situ ring-opening polymerization approach to combine the thermostable hard segment (polybenzoxazine) and the thermoplastic soft segment (polycaprolactone and silver NPs) as the laser trigger. The resulting material presented shape memory, high sensitivity to thermal light, and a low activation energy, which was mainly attributed to the presence of silver NPs.

Shape memory has also been used to develop new smart actuators with fast and reversible changes. An example of this application is reported by Chen *et al.* (2018b), who described the synthesis of hybrid GO/PNIPAm film-based hybrid bilayer actuators. These materials feature reversible bending/unbending behaviors in response to repeated cycles of NIR light irradiations. The NIR photothermal absorption capacity of GOs and the thermal response capacity of PNIPAm are used in these actuators. By irradiating NIR, the GO converts the absorbed energy into heat, which is transmitted to the PNIPAm, causing the chains to collapse. This bending is reversible in the presence/absence of NIR and exhibits a shape memory effect due to the incomplete recovery of PNIPAm chains.

The synthesis of thermoresponsive polymer nanocomposites with shape memory gives rise to countless applications in various areas, since it allows the creation of custom materials with thermal, electrical, mechanical and shape memory characteristics.

Table 2 Applications of thermoresponsive polymer nanocomposites

Thermoresponsive polymer	Nanofiller	Application	Ref.
Poly(<i>N</i> -isopropylacrylamide- <i>co</i> -metacrylic acid)	Mesoporous silica	Insecticide delivery	(Gao <i>et al.</i> , 2020b)
PNIPAm	Hydroxyapatite NPs	Filler for tooth defects	(Tempesti <i>et al.</i> , 2018)
PNIPAm	Graphite oxide NPs	Highly effective adsorbents	(Tian <i>et al.</i> , 2018)
PNIPAm	Silver NPs, silica NPs, and carbon nanotubes	Antimicrobial materials	(Poudel <i>et al.</i> , 2017; Tan <i>et al.</i> , 2018)
PNIPAm	Clay (synthetic hectorite) nanosheets	Synthesis of discrete monometallic (Ag, Au, and Pd) and bimetallic (Pt-Pd, Au-Pd) NPs	(Varade and Haraguchi, 2018)
PNIPAm	Graphene NPs	Therapy and diagnosis	(Seo <i>et al.</i> , 2016)
Poly(<i>N</i> -isopropylacrylamide- <i>co</i> - <i>n</i> -butyl acrylate)-poly(ethylene glycol)-poly(<i>N</i> -isopropylacrylamide- <i>co</i> - <i>n</i> -butyl acrylate)	Silver NPs and GO nanosheets	Wound dressing	(Yan <i>et al.</i> , 2019)
PNIPAm	Silica NPs	Three-dimensional (3D) printing	(Guo <i>et al.</i> , 2019)
Poly(vinyl methyl ether)	GO, antimony, tin oxide and silver NPs	Smart windows	(Kim <i>et al.</i> , 2019)
Poly(<i>N</i> -isopropylacrylamide- <i>co</i> -acrylic acid)	Magnetite NPs	Heavy metal ion recovery	(Hayashi <i>et al.</i> , 2019)
PNIPAm	Polydopamine NPs	Electronic skin	(Di <i>et al.</i> , 2019)
PNIPAm	Nanoclays	Soft robots	(Yao <i>et al.</i> , 2015)
PNIPAm	GO NPs	Intelligence, remote-controlled	(Zhang <i>et al.</i> , 2017)
PNIPAm	GO NPs and hectorite clay	Soft actuators	(Zhang <i>et al.</i> , 2014a)

Other applications

In addition to the applications described above, multiple applications of thermoresponsive polymer nanocomposites have been reported in different areas. Some of the most recent and interesting applications are shown below in [Table 2](#).

Conclusions and Perspectives

Thermoresponsive polymer nanocomposites are materials with diverse applications in biomedicine, aerospace engineering, robotics, environmental science, and the development of new materials. The wide range of applications reported to date is due to the superior ability of these materials to control the response to various stimuli. Many of these properties are enhanced by the use of either inert or active thermoresponsive nanofillers. The reviewed literature shows that progress is being achieved in the development of new synthetic routes and strategic combinations that allow the development of new materials with specific properties for each need.

This article placed a special emphasis on PNIPAM-based nanocomposites, as it is the most commonly investigated thermoresponsive polymer. By modifying the chemical structure of the polymer (copolymerizing) or through the interactions of its chains (with nanofillers), its biocompatibility, biodegradability, and transition temperature have been modified, which may generate a whole new range of nanocomposite materials with a spectrum of new applications in different areas.

Future directions include the development of new materials that react (or not) to the environment, such as the presence of microorganisms, chemical compounds, or various biological variables to which this type of material would be subjected during its application. On the other hand, the mechanical properties must be improved without affecting the thermal response or biocompatibility of the materials, mainly for applications in biomedicine, such as tissue engineering.

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Smart Cellulose Composites: Advanced Applications and Properties Prediction Using Machine Learning

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Nomenclature

ANN Artificial neural networks

BC Bacterial cellulose

CNC Cellulose nanocrystal

CNN Convolutional neural network

GA Genetic algorithms

GF Gauge factor

KNN K-nearest neighbors algorithm

MLR Multiple linear regression

MSE Mean square error

NP Nanoparticle

NW Nanowire

PCA Principal component analysis

PVA Polyvinyl alcohol

RF Random forest

TEMPO 2,2,6,6-tetramethylpiperidine-1-oxyl
((CH₂)₃(CMe₂)₂NO)

Glossary

Chord length distribution It describes size, shape and spatial arrangement of geometrical objects (particles). It can be obtained from a focused beam reflectance measurement (FBRM) probe.

Conductimetric (or conductometric) sensor A sensor that measures changes in capacitance. Humidity is commonly measured with conductimetric sensors using a hydrophilic porous polymer film placed between two electrodes.

Gauge factor Ratio of relative change in electrical resistance, R , to the mechanical strain, ε . In a tensile test, for example, the longitudinal strain corresponds to the change in length divided by the original length.

Shape fixity It quantifies the ability of the switching segment in a material to fix the temporary deformation during the programming process.

Shape memory A property exhibited by certain compounds of recovering their original shape when they are subject to an external stimulus (e.g., temperature change) after having been deformed.

Shape recovery It quantifies the ability of a shape memory material to recover its permanent (original) shape.

Superstretchability Property of a material with exceptional elasticity.

Vitrimer A special class of polymer which combines the properties of thermosets and thermoplastics. They possess crosslinked structure like thermosets but they can be recycled like thermoplastics.

Brief Overview of Cellulose: Structure, Sources, and Main Applications

Cellulose is hydrophilic, biocompatible, biodegradable and, most importantly, the most abundant biopolymer on Earth, with about 1.5 trillion tons of the total annual biomass production worldwide (Chang, 2004). It is a solid, linear syndiotactic homopolymer composed of D-anhydroglucopyranose units linked by β -(1 $\rightarrow$ 4) glycosidic bonds. These chains are organized into elementary fibrils (nanosized fibers), which aggregate into larger structures called microfibrils (Rongpipi *et al.*, 2019). Both amorphous and crystalline domains are present in the microfibrils and variations in the volume fraction of the crystalline counterpart and crystal size determine the differences in morphology, mechanical properties, and thermal stability of the microfibril and, in turn, of the final cellulosic product.

There are quite many cellulose sources including wood fibers, tunicates, algae, and some bacteria. Cellulose has been traditionally used to produce paperboard and printing/writing paper and can be processed in several forms such as fibers, film/membrane, polymer, and nanocomposites (Qiu and Hu, 2013). Raw cellulose fibers purified or extracted from cellulose sources can be subject to mechanical pressure, acid hydrolysis, or enzymatic treatment followed by high-pressure homogenization to yield microfibrillated, nanofibrillated cellulose (Schütz *et al.*, 2012) and, more recently, cellulose nanocrystals (CNCs).

CNCs have gained much attention within the scientific community as fillers in smart composites. CNCs are rod-like nanoparticles (NPs) that can be extracted from cellulosic material by acid hydrolysis, sonochemical fragmentation, microbial or enzymatic digestion, among others (Sacui *et al.*, 2014). The exact shape and dimensions of the CNCs depend on the preparation method and conditions. Generally, they are 3–5 nm in width and 100–300 nm in length.

The so-called bacterial cellulose (BC) is obtained from the fermentation of sugar in Gram-negative bacteria (*Acetobacter xylinum*). BC is characterized by a crystalline nanofibrillar structure able to retain a large amount of liquid due to its large surface

area (Silva *et al.*, 2017). For this reason, it has been proposed as a wound material to treat damaged epithelial tissues because it is foldable, and it has high water-holding ability and mechanical strength in the wet state (Anton-Sales *et al.*, 2019).

Cellulose in Smart Composites

Cellulose-containing materials can be obtained via chemical modifications of the cellulose structure or via its incorporation/blending with other compounds. The latter is typically pursued to obtain composites in which cellulose acts either as matrix, filler, or coating/shell. Cellulose composites find uses as biomaterial, reinforcement material, barrier film, membrane, and drug delivery, among others. The preparation, properties and applications of smart cellulose-based materials were reviewed by Qiu and Hu in the past, covering the 2002–2012 decade (Qiu and Hu, 2013). In their review, the use of cellulose as matrix in glucose-, temperature, and vapor-responsive membranes, as filler in the form of CNCs, and as coating or shell of microspheres was surveyed. In the present article, current applications of smart cellulose-containing composites are overviewed, and illustrative examples are provided.

Shape-memory Applications

Smart materials have been traditionally based on smart polymers, which often respond to a wide range of external stimuli thanks to the responsive character of their moieties, often incorporated on purpose (Aguilar and San Román, 2019). The result of combining a smart polymer with another component that either modifies the responsive behavior or adds additional functionalities to the material is referred to as smart hybrid system. CNCs have found uses in smart hybrid systems as they can endow the final material with mechanical and optical functionalities. In this respect, the development of smart, polymer-based hybrid systems incorporating CNCs has been the subject of intensive research in the last years. The use of CNCs in physically (thermo-, pH- and multi-responsive) systems and optically (mechano- and humidity-responsive) photonic systems, as well as self-healable, and shape-memory composites have been recently reviewed by Nasseri *et al.* (2020).

Cellulose composites with water-active shape-memory properties have been proposed for minimally invasive medical devices. In this case, shape-switching is achieved through water absorption/desorption rather than by temperature. Since the pioneering work from Weder with cellulose nanofibers (Capadona *et al.*, 2008), a number of cellulosic materials have been integrated into polymer matrices such as poly(D,L-lactide), poly(glycerol sebacate urethane), polyurethane, poly(propylene carbonate) to obtain water-responsive shape-memory properties (Wang *et al.*, 2018). For example, Wu *et al.* combined biodegradable poly(glycerol sebacate urethane) (PGSU) elastomer with varying amounts of CNCs (Wu *et al.*, 2014). Quasi-static mechanical testing of the PGSU-CNC composites showed that the addition of CNCs to PGSU increased the tensile strength from 3.91 to 12.4 MPa, providing an efficient stress transfer from the PGSU (matrix) to the CNCs (filler). Dynamic mechanical analysis was used to demonstrate the softening effect of water on the nanocomposites. These exhibited water-responsive mechanically adaptive properties. In particular, the storage modulus (E') could be reversibly changed upon exposure/removal of water. Best shape-memory response was achieved for composites containing 23.2 vol% CNCs, which showed shape recovery (R_r) and shape fixity (R_f) ratios of 98% and 99%, respectively. Current efforts are directed towards increasing the response rate of the composites (Wang *et al.*, 2018).

Recently, cellulose has been combined with vitrimers to render a new class of strong and smart composites. Vitrimers are considered the third category of polymeric materials and derive from thermosets. Opposed to thermosets, however, the networks of vitrimers are not permanent and can be tuned via thermally induced exchange interactions between different positions in the polymer chain. Using natural cellulose paper as a reinforcing framework, Chinese scientists infiltrated and directly polymerized into the cellulose paper two bio-derived monomers (bis(6-membered cyclic carbonate) and 1,3-propanediol), yielding a polycarbonate-cellulose composite named “vitri-mer paper” (Zhao *et al.*, 2019). The shape-memory properties of the vitri-mer paper were first examined in air. Fig. 1 shows the sequence of steps of a paper stripe from room temperature to 150°C and back to room temperature. If the stripe is shaped into a helix at 150°C, the helicoidal shape remains when the temperature is decreased to room temperature. If the temperature is then again increased to 150°C, the helix rapidly transforms into its original flat state. The process of shaping and reshaping can be repeated with the same heating-cooling sequence over and over. Authors also demonstrated that shape-memory properties could also develop in liquid environment (namely, neutral water, acidic and alkaline water, and even dimethyl sulfoxide). Interestingly, the vitri-mer paper showed self-healing properties towards surface scratches and could be fully degraded by acid hydrolysis followed by decarboxylation, making it a green, and sustainable composite.

Wearable Technology Applications

Cellulose is often combined with graphene-based materials to produce smart wearable sensing composites that translate external mechanical stimuli like strain and pressure into changes in their electrical resistance (Yan *et al.*, 2014; Chen *et al.*, 2018; Wu *et al.*, 2018). Liu *et al.* (2019) created a network of graphene nanoplates within cellulose by coating and hot pressing a dispersion of the former in polyvinylpyrrolidone. The resulting nanocomposites showed a Gauge factor (GF) of 5.86 and short response times to applied strain and pressure, suggesting that the distances between adjacent nanoplatelets changed in a very reproducible manner according to the connection-disconnection effect. According to it, some of the original connected graphene nanoplates would lose overlapping areas and disconnect upon stretching, causing an increase of the electrical resistance, whereas the overlapping areas

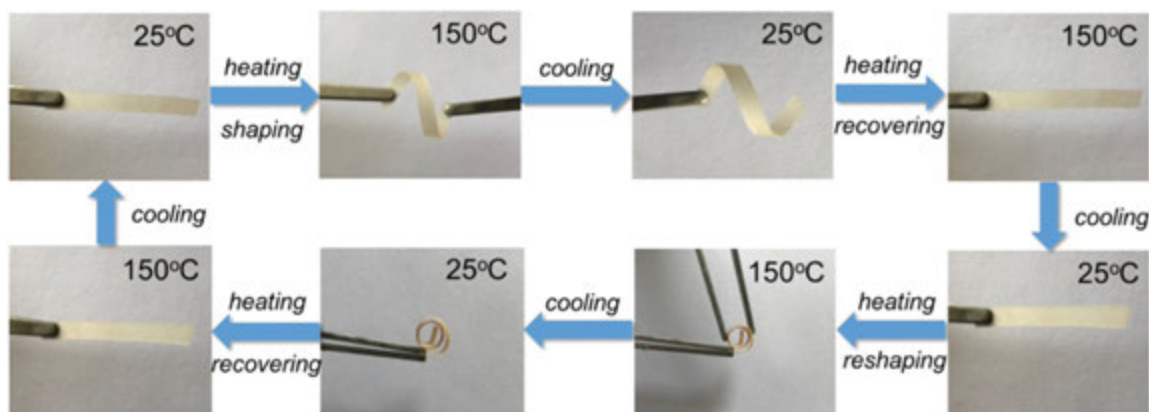


Fig. 1 Shape-memory and reshaping properties of a vitrimer-paper composite. Reprinted with permission from Zhao, W., Feng, Z., Liang, Z., *et al.*, 2019. Vitrimer-cellulose paper composites: A new class of strong, smart, green, and sustainable materials. *ACS Applied Materials Interfaces* 11, 36090–36099.

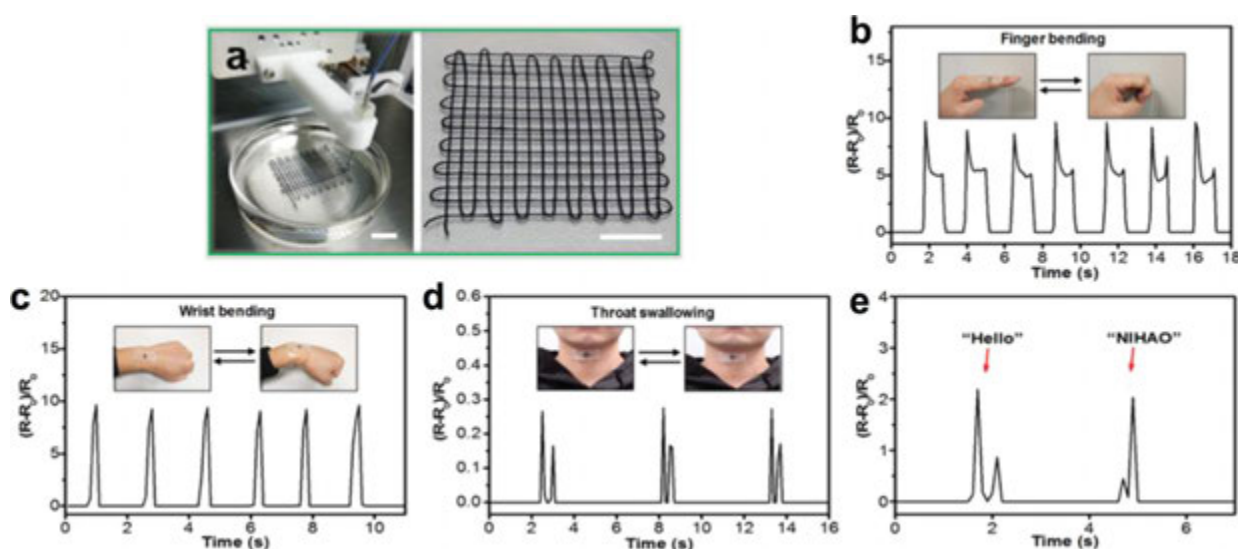


Fig. 2 (a) Optical image of the 3D-printed TOCNFs/Ti₃C₂ fabrics with a woodpile structure. Relative resistance changes of the composite fabrics on (b) finger bending, (c) wrist bending, (d) swallows of the throat, and (e) speaking “Hello” and “NIHAO”. The scale bar in (a) is 1 cm. Reprinted with permission from Cao, W.-T., Ma, C., Mao, D.-S., *et al.*, 2019. MXene-reinforced cellulose nanofibril inks for 3D-printed smart fibers and textiles. *Advanced Materials* 29, 1905898.

and connection points would increase back upon compressing, thereby causing a decrease of the electrical resistance (Liu *et al.*, 2018; Wang *et al.*, 2020). Importantly, the composites withstood 1000 loading/unloading stretching cycles thanks to the strong interfacial adhesion between cellulose and the graphene nanoplates, with a minor variation in resistance of 3 Ω cm due to the residual deformation of the cellulose matrix (Liu *et al.*, 2019). 2D materials other than graphene have also been combined with cellulose to produce sensitive strain sensors. Cao *et al.* fabricated smart fibers and textiles by 3D printing with hybrid inks consisting of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidized cellulose nanofibrils and Ti₃C₂ transition metal carbide nanosheets (referred to as MXenes, Fig. 2(a)) (Cao *et al.*, 2019). The tensile stress-strain curves of the composite printed fibers showed that the addition of the Ti₃C₂ nanosheets resulted in an increase of both the tensile strength and Young's modulus from 86.8 MPa and 4.5 GPa, respectively, for the Ti₃C₂-free TEMPO-mediated oxidized cellulose to 136.5 MPa and to 9.3 GPa, respectively, for the TEMPO-mediated oxidized cellulose with 30 wt% Ti₃C₂. The electrical conductivity could be tuned as well with the addition of MXenes to cellulose. The composite fibers exhibited both photothermal and electrothermal properties, making them amenable as wearable heaters with outstanding Joule heating performance under safe input voltage. A textile strain sensor fabricated with the composite material and tested at a strain rate of 1.3 mm s⁻¹ under several cycles reached impressive GF values of 87.8 and 399.5 within the strain range of 4%–8% and 8%–10%, respectively. Its use as a skin-based wearable device for the real-time detection of human motion and physiological signals was proven upon attaching it on finger, wrist, and throat (Fig. 2(b–e)).

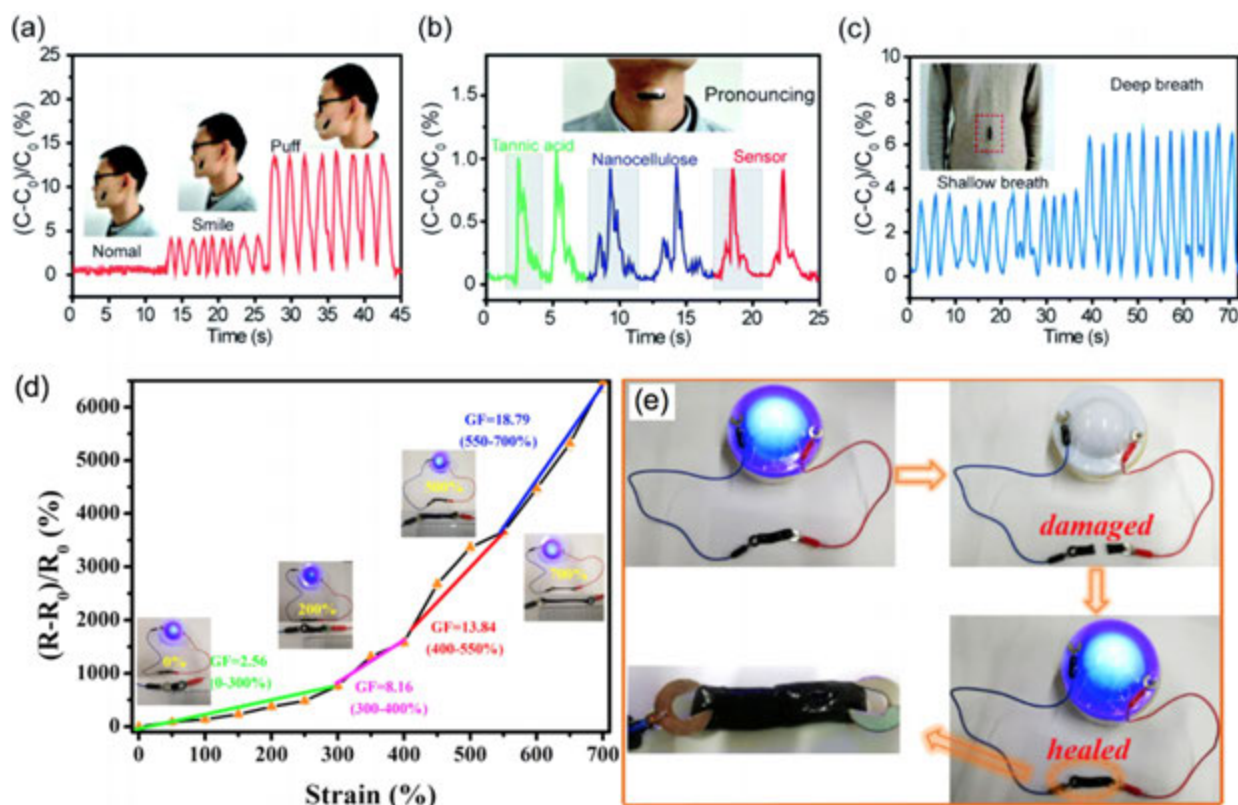


Fig. 3 Performance of hydrogel-based sensors containing CNCs, Ag NWs, PVA and tannic acid towards detecting various tiny motions and their self-healing performance: (a) Capacitance signal from face expression; (b) capacitance variations on speaking “tannic acid”, “nanocellulose”, and “sensor”, and (c) capacitance signal originated from different respiration rates. Performance of hydrogel-based sensors containing CNCs, PANI and PVA: (d) Relative resistance variation, $(R-R_0)/R_0$, of 5 wt% CNC-PANI/PVA hydrogel at different strains (where R_0 is the resistance of the hydrogel under no stretching and R is the resistance under stretching) and (e) Luminance variation of an LED during cutting and self-healing processes of the same hydrogel. Reprinted with permission from (a–c) Lin, F., Wang, Z., Shen, Y., *et al.*, 2019. Natural skin-inspired versatile cellulose biomimetic hydrogels. *Journal of Materials Chemistry A* 7, 26442–26455. (d, e) Song, M., Yu, H., Zhu, J., *et al.*, 2020. Constructing stimuli-free self-healing, robust and ultrasensitive biocompatible hydrogel sensors with conductive cellulose nanocrystals. *Chemical Engineering Journal* 398, 125547.

In the field of wearable technology, the incorporation of metallic nanowires (NWs) within the fibers of cellulosic paper is currently a blooming area of research. Metallic NWs endow paper with electric conductivity and thermal dispersion capability. For example, Li *et al.* (2019) produced interconnected Ag NWs networks within the cellulose structure by dip coating followed by thermal annealing. The resulting composite sheet was applied to monitor microstructural changes and human motion with high sensitivity (response and relaxation time of ca. 100 ms) and stability (> 2000 bending/stretching cycles). Importantly, the thermal dispersion capacity of the composite allowed removing redundant heat, thereby prolonging the lifetime of the device. 3D printing with cellulose nanofibers and Ag NWs inks on polyimide film has been also carried out to obtain ion selective sensor system towards ammonium ion (Kim *et al.*, 2019).

Hydrogels are another sort of attractive materials with which cellulose can be blended (Lu *et al.*, 2017). Different definitions for hydrogels have been put forward in the literature. Perhaps the most intuitive one is that hydrogel is a polymeric material with the ability to swell and retain a significant fraction of water within its structure, but without dissolving in water (Ahmed, 2015). CNCs decorated with tannic acid and Ag NPs were mixed with polyvinyl alcohol (PVA) hydrogel to obtain a multifunctional single structure characterized by superstretchability, self-adhesion to various surfaces, self-healing capability, conformability, and strain sensing performance based on variations in the capacitance of the device (Lin *et al.*, 2019). The latter was constructed by sandwiching a dielectric layer within two composite hydrogel layers. Fig. 3(a–c) illustrates the sensitivity of the biomimetic capacitance sensor to human smiling and puffing, pronunciation of some selected words, and shallow/deep breathing.

Branched CNCs were also combined with polyaniline (PANI) and PVA to yield conductive biomimetic hydrogels with large tensile strength (171 KPa), superstretchability (1085%), self-healing (up to 99.6% within 120 s in both air and underwater) performance, adhesive properties, and sensitivity to human motions (Song *et al.*, 2020). Enhanced mechanical toughness of these skin-like composite hydrogels was achieved by populating the CNCs with a large density of polycarboxylic groups via grafting with citric acid and ascorbic acid, which precluded PANI aggregation during polymerization of aniline in the synthesis phase. The strain sensing performance of the hydrogel is illustrated in Fig. 3(d), which shows that $(R-R_0)/R$ increases with the strain due to the increase in the distance of PANI networks upon stretching. The GF of the hydrogel increased from 2.56 ($0\% < \varepsilon < 300\%$) to 18.79

($550\% < \varepsilon < 700\%$), indicating high strain sensitivity and hyperextension. The insets, which show pictures of the hydrogel illuminating a LED bulb in a closed-loop, prove that the hydrogel maintains the electrical conductivity in spite of being severely stretched. Importantly, if the hydrogel is cut into two pieces, the light goes off. After self-healing in 30 s, the light bulb goes on again (Fig. 3(e)).

Hydrogels can also be printed from inks with a suitable rheology. For example, Lewis *et al.* were able to do so with composite hydrogel architectures encoded with localized, anisotropic swelling behavior controlled by the alignment of cellulose fibrils along prescribed four-dimensional (4D) printing pathways (Gladman *et al.*, 2016). This research paved the way toward programmable fabrication of plant-inspired architectures as complex as orchid flowers able to change their shape on immersion in water.

Food Packaging Applications

In the frame of circular economy, food packaging is undeniably one of the timely applications of cellulose. Regenerated cellulose is expected to replace traditional, non-degradable synthetic plastics used in food packaging, which have posed severe environmental concerns. Cellulose films offer good barrier properties to maintain the freshness of products, mechanical robustness, biodegradability, and recyclability. Gu *et al.* dissolved cotton fibers using an alkalized urea solution and further destroyed the bond between C2 and C3 of the cellulose ring with IO_4^- to form adjacent aldehyde groups by oxidation. An hyperbranched polyamide-amine (HPAMAM) hybrid was used to grow Ag NPs in situ and, finally, the HPAMAM-capped Ag NPs were grafted onto the oxidized cellulose through the aldehyde groups (Gu *et al.*, 2020). Since mechanical robustness is required in food packaging applications, the mechanical properties of the composites were evaluated. Tensile strength and strain of the composite films increased with the amount of HPAMAM-capped Ag NPs grafted to the oxidized cellulose, surpassing the values of non-grafted oxidized cellulose film. After the antibacterial effect originating from the Ag NPs was proven with *Escherichia coli* and *Staphylococcus aureus*, cherry tomatoes were wrapped with the composite film, non-oxidized and oxidized cellulose films, and commercial polyethylene film. The tomatoes protected with the composite film kept their freshness after 9 days, whereas the cherries wrapped with the other three were decayed and mycelium attached to their surface (Fig. 4).

Nanocellulose and BNC have also been used in composites for intelligent food packaging. For example, Vilela *et al.* produced an intelligent food package by combining BNC and poly(sulfobetaine methacrylate) (PSBMA) with acceptable protonic conductivity thanks to the presence of sulfonic groups in the PSBMA structure (Vilela *et al.*, 2019). Proton motion plays an important role in conductimetric humidity sensors by detecting humidity levels in foodstuff that cannot withstand high environmental humidity such as dry foods, dairy and meat products.

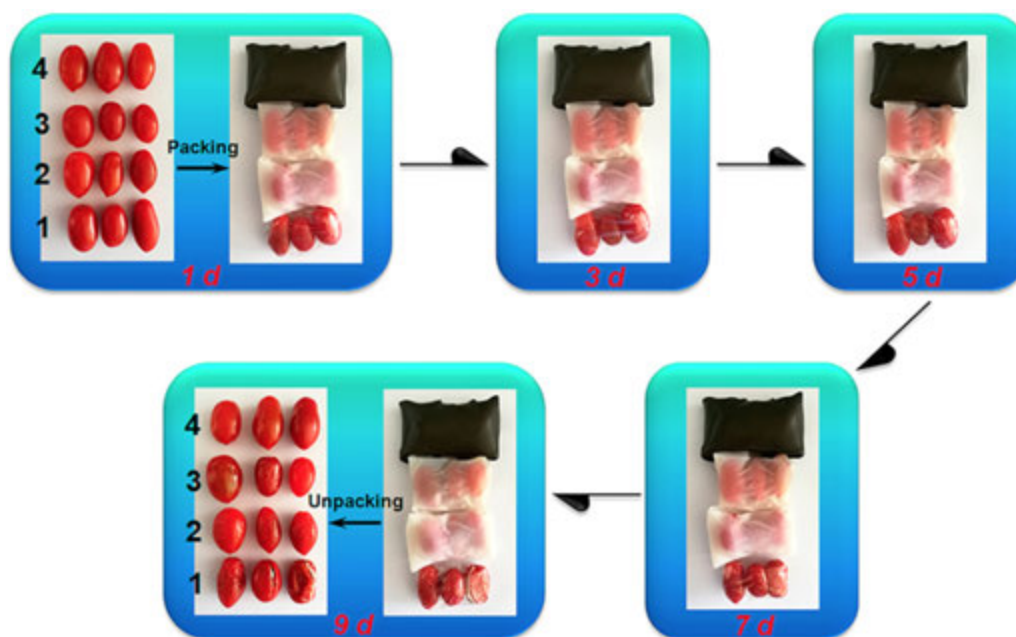


Fig. 4 Storage study of Ag@HPAMAM NPs-embedded cellulose film. Cherry tomatoes in 1, 2, 3, and 4 groups were wrapped in commercial polyethylene, cellulose, oxidized cellulose, and Ag@HPAMAM NPs-embedded cellulose films, respectively. Comparison of the macroscopic appearance of the cherry tomatoes for the different groups after storage at constant temperature and humidity (25°C, 75% relative humidity) for 1, 3, 5, 7, and 9 days. The concentration of Ag@HPAMAM NPs in the film of group 4 was 2.0 mM. Reprinted with permission from Gu, R., Yun, H., Chen, L., Wang, Q., Huang, X., 2020. Regenerated cellulose films with amino-terminated hyperbranched polyamic anchored nanosilver for active food packaging. *ACS Applied Bio Materials* 3, 602–610.

Table 1 Recently published, exemplary reviews on smart composites, fully or partially covering cellulose hybrids

Topic	References
Applications of mixed materials of cellulose, nanocellulose and carbon nanotubes. Smart applications are covered	Miyashiro <i>et al.</i> (2020)
Hydrogel sensors and actuators. Examples of hydrogel machines involving cellulose are provided	Liu <i>et al.</i> (2020)
Smart cellulose-based nanomaterials. Includes a comprehensive table that compares different stimuli-responsive cellulose nanomaterials, their fabrication techniques, response mechanisms, and potential applications	Zhu <i>et al.</i> (2020)
Smart CNC based composites	Nasseri <i>et al.</i> (2020)
Cellulose paper composites for light harvesting and sensing applications	Vicente <i>et al.</i> (2018)
Nanocellulose/nanocarbon composites for biotechnology and medicine applications	Bacakova <i>et al.</i> (2020)

Other Smart Applications

The use of cellulose in thin film optoelectronic applications is quite recent. In this line, a number of studies in which cellulose paper is used for light harvesting has been put forward (Vicente *et al.*, 2018). Cellulose-based materials can be engineered into ideal substrates with flat surface, good mechanical and chemical stability, thus competing with tradition substrates used in optoelectronic devices. Paper–cellulose fibers are its most important constituent– can be regarded as a bendable mechanical support that can be processed on purpose to exhibit high transparency and haze to enhance light transmission and coupling. On the other hand, the integration of cellulose-based materials in the set-up constituents of electrochemical energy conversion and storage devices (e.g., lithium ion batteries or supercapacitors) is currently blooming and will see a huge increase in the forthcoming years (Dutta *et al.*, 2017; Wang *et al.*, 2017; Chen *et al.*, 2020).

For completeness, Table 1 lists a selection of reviews published within the last three years in the field of cellulose-containing smart composites.

Machine Learning Meets Materials Science – The Case of Cellulose Composites

As the incursion of machine and deep learning methods into the materials science field is quite recent, applications are not sophisticated but rather basic and so does the algorithms used, as opposed to other fields in which machine and deep learning are more widely spread and intensified such as computer vision (Khan and Al-Habsi, 2020), signal processing (Purwins *et al.*, 2019), action recognition (Wu *et al.*, 2017) or medical image analysis (Torrents-Barrena *et al.*, 2019). Therefore, a myriad of works integrating machine and deep learning into solid-state science will likely appear in the forthcoming years. Computational algorithms that improve automatically through experience are at the core of machine and deep learning. Hence, one needs to combine a reasonably large sample data referred to as “training data” with strong computing power in order to screen for the ideal experimental candidates or conditions leading to improved material performance. With this philosophy in mind, the discovery of new materials (Cai *et al.*, 2020) and the calculation of multiple material properties (Schmidt *et al.*, 2019) have been realized so far. The main bottleneck of machine and deep learning in materials science is the size of the training dataset, which compromises their success (leading to either underfitting or overfitting). Machine and deep learning can be divided into three main categories; namely, supervised learning, unsupervised learning, and reinforcement learning. The first one tries to find the unknown function that connects known inputs to unknown outputs as a standard fitting procedure. Unsupervised learning is based on finding patterns in unlabeled data, as, e.g., in the clustering of samples. Finally, reinforcement learning is concerned about achieving a goal or taking good actions in an environment in order to maximize a reward. In other words, it learns from interactions. Supervised learning is the main approach followed in materials science. Since obtaining some material properties is often related to costly experimental methods, which preclude the availability of large datasets, publicly available material datasets like the materials project (Jain *et al.*, 2013), the inorganic crystal structure database (Allen *et al.*, 1987), the Open Quantum Materials database (Kirklin *et al.*, 2015), the NOMAD archive (Draxl and Scheffler, 2018), and the SuperCon (Stanev *et al.*, 2018), among others, have been used. Yet, the success of machine and deep learning in materials science will rely on the ease to obtain large amounts of data in a costly and time efficient manner.

Brief Overview of Machine Learning Techniques Applied to the Study of Cellulose and Cellulose Composites

Traditional machine and deep learning methods encompass linear and nonlinear regression, artificial (convolutional) neural networks, decision trees, random forests, clustering, support vector machines, and genetic algorithms (Winkler, 2020), among others. In this section, we briefly introduce the machine and deep learning techniques that have been applied so far to the field of cellulose composites, as overviewed further in Section “Machine Learning Applied to Cellulose Composites”.

Multiple linear regression (MLR)

Multiple linear regression (MLR) is a statistical technique aimed at modeling the linear relationship between explanatory (independent) variables and response (dependent) variable (Freedman, 2009). MLR is the extension of the so-called ordinary least-squares regression, in which just one independent variable is used. Here, MLR makes use of multiple independent variables to predict the outcome of a response variable. The MLR assumes that the independent variables are not too highly correlated with

each other. In turn, these are selected independently and randomly from the population. The model's error term (known as the residuals) should exhibit a normal distribution with a mean 0 and a variance σ .

K-nearest neighbors algorithm (KNN)

The KNN algorithm is a non-parametric approach utilized for classification and regression tasks (Altman, 1992). The input consists of the K closest samples in the feature space. Depending on whether classification or regression is performed, the testing sample is (1) categorized using a voting schema among neighbors, with the sample being assigned to the most predicted class, or (2) computed as the mean of the neighbors' values.

More specifically, the KNN method is based on instance learning (*a.k.a.* lazy learning), where the function is approximated locally and all calculation is deferred until function assessment. Since the classification approach relies on distance, normalizing the training set can greatly improve the overall performance. The metrics employed for continuous and discrete variables are Euclidean and Hamming distances, respectively. A useful technique for both classification and regression purposes is to assign proportional weights to the contribution of neighbors, so that the nearest contribute more to the final evaluation. The neighbors are taken from a set of samples for which the class (classification) or the sample property value (regression) is known. The KNN methodology is sensitive to the local structure of the data.

Random forest (RF)

Random forest (RF) is a supervised classification or regression algorithm (Ho, 1995) that has good predictive performance with relatively little hyperparameter tuning. It is an ensemble learning approach that operates by building multiple decision trees, normally trained with bagging, and calculating the inferred class or mean prediction of the individual trees. Bagging often considers homogeneous weak classifiers that learn independently (and simultaneously) from each other. Their output is subsequently combined through a deterministic averaging procedure to increase the overall accuracy. RF generally outperforms decision trees, but their performance is lower than gradient boosted trees.

RF reduces tree correlation by injecting randomness into the tree-growing procedure. Concretely, it conducts split-variable randomization each time a division is to be done during the bagging approach. RF thus searches for the best feature among a random subset while splitting a node, which results in a wide diversity that usually produces better (robust) models. The basic algorithm for a regression or classification RF can be generalized as follows:

-
1. Given a training dataset:
 2. Select number of trees to build (n_trees)
 3. for $i = 1$ to n_trees do
 - 3.1 Generate a bootstrap sample of the original data
 - 3.2 Grow a regression/classification tree to the bootstrapped data
 4. for each split do
 - 4.1 Select m_try variables at random from all variables
 - 4.2 Pick the best variable/split-point among the m_try
 - 4.3 Split the node into two child nodes
 - end
 5. Use typical tree model stopping criteria to determine when a tree
 - Is complete (but do not prune)
 - end
 6. Output ensemble of trees
-

Principal component analysis (PCA)

Dimensionality reduction methodologies focus on lowering the feature space, thus allowing most of the information or variability in the data to be described using fewer features (or components).

Principal components analysis (PCA) was firstly proposed by Pearson (1901). It is an algorithm for finding uncorrelated low-dimensional representations of data that retain the original dissimilarity. The idea is that each of the n observations lives in p -dimensional space, but not all dimensions are equally significant. The new dimensions found in PCA are linear combinations of the original p features. A small (and rich) subset of feature dimensions will thus be employed in further analyses while retaining most of the information present in the parent data. Such reduction can help define many features in the database and eliminate multicollinearity, which often improves predictive accuracy in downstream supervised models. PCA can be computed using different algorithms including Eigen analysis, latent variable analysis, factor analysis, linear regression or singular value decomposition (SVD). Of them, the latter is the most widely utilized approach.

Artificial neural networks (ANN)

Artificial neural networks (ANN) endeavor to recognize underlying relationships in a data space by mimicking the way the human (animal) brain operates (Hinton and Salakhutdinov, 2006). In this sense, they rely on connected units or nodes called artificial neurons, which aim to model the biological neurons. ANN-based systems have essentially three layers: (1) an input layer, which collects the original input features, (2) a hidden layer, in which the learning process takes place, and (3) the last layer that infers the output results (Fig. 5). Additionally, the biologic neuron receives inputs from many adjacent neurons. When these inputs

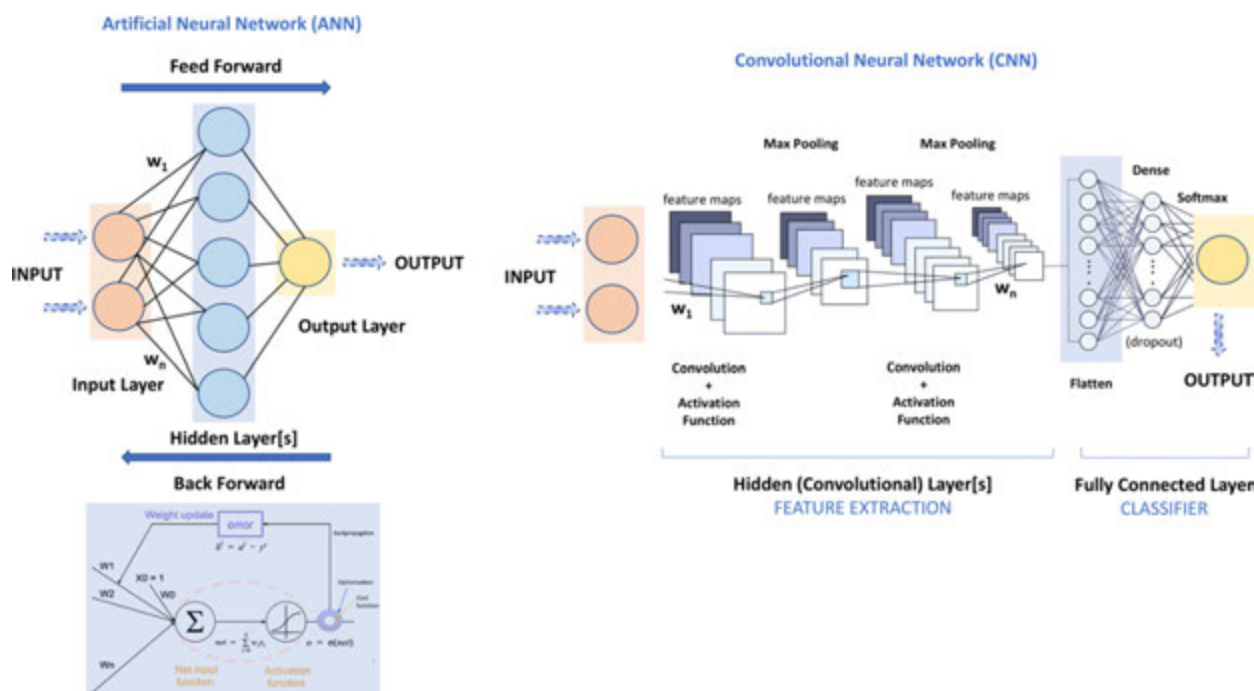


Fig. 5 Schematics of the architectures for ANNs and CNNs.

accumulate beyond a certain threshold the neuron is activated suggesting there is a signal. ANNs work in a similar fashion using non-linear activation functions (e.g., sigmoid, softmax, rectified linear unit).

On the forward pass, the ANN selects a batch of features, randomly assigns weights across all the node connections, and predicts the output. The backpropagation algorithm, which uses a loss function (to measure the performance) and an optimizer, is applied to automatically adjust the weights. On the backward pass, the gradient of the loss is calculated with regards to the network weights, the weights are adjusted a little in the opposite direction of the gradient, another batch of features is grabbed, and the process is repeated until loss minimization (*a.k.a.* mini-batch stochastic gradient descent).

In deep learning, convolutional neural networks (CNN) are very similar to ordinary ANNs as they are made of neurons that have learnable weights and biases (Emmert-Streib *et al.*, 2020). Nevertheless, CNNs have one or more convolutional layers that consider the context (shared information) in small neighborhoods and reduce the number of units (fewer parameters) across the whole network (Fig. 5).

Genetic algorithms (GA)

A genetic algorithm (GA) is a metaheuristic for solving both constrained and unconstrained optimization and search problems based on a natural selection procedure that mimics biological evolution (Jennings *et al.*, 2019). The fittest individuals are thus nominated for reproduction to produce the next generation. GA methodologies (1) work with a coding of the parameter set, (2) utilize payoff information (not derivatives), and (3) employ probabilistic transition rules (not deterministic). The main GA operators are:

- *Reproduction* is based on the fitness function, which identifies how “good” an individual is. Individuals with higher fitness have more probability of contributing to the next generation.
- *Crossover* is a process in which members of the last population are mated randomly. Individuals born from two different parents with enhanced fitness are combined.
- *Mutation* does a random walk through the coded parameter space to ensure that relevant information contained within individuals may not be lost prematurely.

The evolution (encoded as an iterative process) initiates from a random population. The individual’s fitness is assessed in each generation, and the ones with higher values are stochastically chosen. The individuals are then recombined (and possibly randomly mutated) to produce a new generation, which will be utilized in the next iteration. The evolution finishes when either a maximum number of generations is created, or an acceptable fitness is reached for the population.

Machine Learning Applied to Cellulose Composites

Several works in the literature used neural models in papermaking, specifically to predict paper properties (Scharcanski and Dodson, 1996; Gyaneshwar *et al.*, 2000; Olejnik and Ciesielski, 2004; Nieminen *et al.*, 2011; Ciesielski and Olejnik, 2014) and for

pulping process control (Dayal *et al.*, 1994; Zhu *et al.*, 1997). More recently, neural models have been applied to cellulose refining step, which is critical in paper production. During refining (mechanical treatment of their water suspensions), fiber flocs undergo compression and shear forces that change several fiber characteristics such as morphology and distribution of chemicals on their surface. Almonti *et al.* (2019) predicted the fibers length through an ANN fed with (1) the fibers typology and refiner geometry variables, and (2) three principal components calculated from the PCA and single-linkage hierarchical clustering of the pulp flow, fibers length, fillers amount, wear rate and refining power parameters. The three-layered ANN, in which the input, hidden and output layers had 11, 7 and 1 neurons, respectively, was trained using the Levenberg-Marquardt algorithm, 52 patterns (70% of data selected randomly) and 2000 epochs. The mean error obtained was 1.07% with a standard deviation of 0.5. Also, the R^2 (coefficient of determination) of 0.98 and the ANOVA analysis (P -value = 1.3317×10^{-11} , F -value = 387.57) indicated that the built model was robust and generalized well.

Vafaenezhad *et al.* (2016) adopted an ANN-GA-based method to fabricate wood-derived carbon matrix composites with maximum compressive strength. This approach was proposed as an alternative to time-consuming X-ray diffraction used for monitoring temperature transformations of carbon during carbonization of wood samples. The wood density, carbonization temperature and time were the network inputs. 36 samples (70% of data) were scaled and normalized between [0,1] before training the three-layered ANN (15, 10 and 1 neurons per layer) with the Levenberg-Marquardt and mean square error (MSE) functions for 100 epochs. Afterwards, the compressive behavior of the composite was estimated using a GA coupled with the trained ANN. The population size, number of generations and elite individuals, crossover fraction and selection function were 1000, 200, 2, 0.6 and stochastic uniform, respectively. In this way, the threshold temperature for amorphous carbon formation, whose presence was related to maximum compression strength of the composites, was determined. Despite minor overfitting, identifiable in average absolute errors, a maximum compressive strength of 38.99 MPa was reached with carbonization temperature, time period and starting material density of 965.3°C, 2.45 h and 0.735 g cm⁻³, respectively. The average absolute and relative errors were 7.84% and -3.48%, and the R^2 was 0.92. This approach eliminates time-consuming characterizations, and consequently, reduces manufacturing costs.

Interestingly, the effect of film-forming PVA and two crosslinkers, namely organic glyoxal (Gx) and inorganic ammonium zirconium carbonate (AZC), on the optical and surface properties of films produced from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibers was investigated by Özkan *et al.* (2018). Aiming at the design of custom-made nanocellulose-based substrates, RFs were utilized to predict surface roughness, contact angle and optical transmittance of films derived from two-component films of cellulose with PVA, Gx or AZC, and ternary combinations of cellulose, PVA and one of the cross-linkers. The mean absolute percentage errors were 4.9%, 3.9% and 0.3%, respectively, for surface roughness, contact angle and optical transmittance. Lately, Özkan *et al.* (2019) implemented an ANN, RFs and MLR to estimate the mechanical properties of nanocomposite films containing the three components (PVA, Gx and AZC) using as input the mechanical properties of two-component films and cellulose-based mono-component films obtained from experimental stress-strain curves. The tensile strength was predicted more accurately by ANN and RF compared to MLR (Fig. 6(a)). Meanwhile, the prediction of Young's modulus improved in the following order: ANN < MLR < RF (Fig. 6(b)). Finally, MLR rendered best prediction for elongation. Overall, the ANN outperformed RF and MLR in terms of mean absolute (percentage) errors and root MSE.

Machine learning has attracted the interest of researchers working in the field of colloid chemistry, more specifically in flocculating agents. For example, Campano *et al.* (2019) proposed the used of cationic hairy cellulose nanocrystals (CNCC) as a flocculant of clay particles, taking kaolinite as a model. Authors employed a RF regression model to estimate fractal dimension from chord length distribution data and, in turn, describe the flocculation process. The fractal dimension values suggested a relationship between floc conformation and CNCC dosage. Specifically, fastest flocculation was found for CNCC doses within the 10–30 mg/g range, corresponding to the isoelectric point of the clay/CNCC system. Details on the methodology followed to implement the RF regression system can be found in a previous study from the same group (Lopez-Exposito *et al.*, 2019). In this study, authors applied an identical machine learning approach to approximate the average fractal dimension of freshwater green microalga *Chlorella sorokiniana* flocs based on correlating the suspension chord length distribution with their average geometry. Importantly, pre-concentration of microalgal cultures through flocculation can reduce the harvesting costs of biomass. The data required to train and optimize the RF regression system was generated using a computer software. A set of (virtual) flocs of prescribed fractal dimension were subject to chord length data acquisition through another software that simulated a beam reflectance probe. Such model was then validated with real data of known average geometry.

Biocompatibility and biodegradability are remarkable features of bio-composites designed to reduce and replace conventional non-biodegradable polymeric materials. Recently, Daghigh *et al.* (2020) applied two KNN approaches, namely, uniform distribution of weights and inverse of distances of weights, to develop lightweight and cost-effective materials by predicting the heat deflection temperatures of poly(propylene)/ethylene-propylene-diene-monomer (PP/EPDM) bio-composites. The selection of K (neighbor number) = 3 using cross-validation offered the best model performance (R^2 = 0.898, mean absolute error = 1.24 and root MSE = 1.583), and suggested that reinforcement components added to the PP/EPDM composites, i.e., short latania fibers, nano-clays, and two ligno-cellulosic agricultural wastes (namely, date seeds and pistachio shells), influenced the heat deflection temperature.

Creating new structural materials with enhanced mechanical properties while still being economically efficient is one of the ultimate goals of modern engineering applications (Chen and Gu, 2019). However, the architectures of biomaterials cannot be

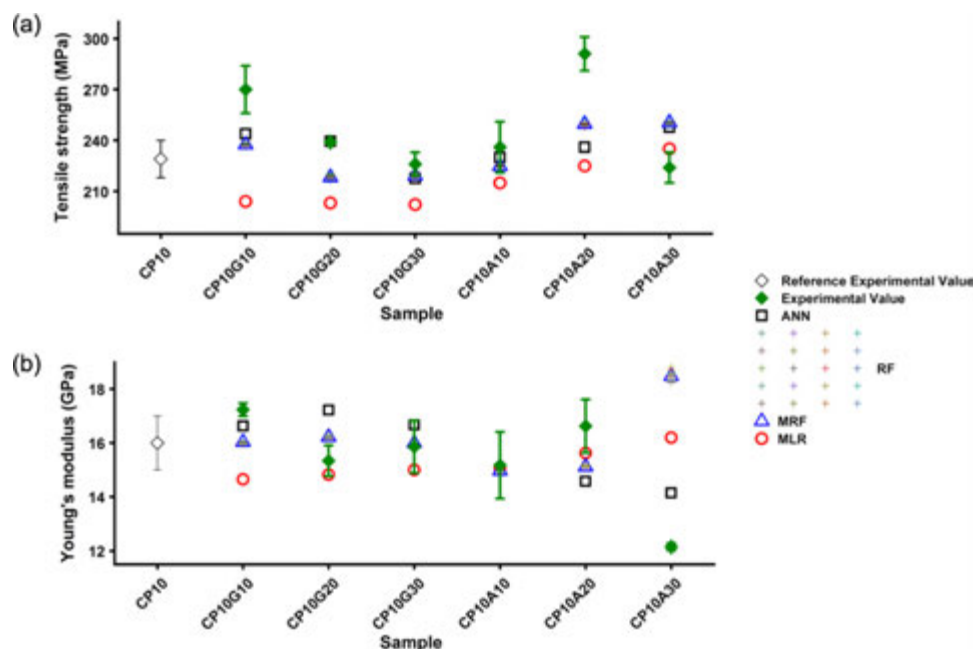


Fig. 6 Experimental values of (a) tensile strength and (b) Young's modulus along with ANN, MLR, and RF prediction results for nanocomposite cellulose films. Nomenclature: "C" stands for TEMPO-oxidized cellulose nanofibers (TOCNFs), "P" for PVA, "G" for glyoxal and "A" for ammonium zirconium carbonate. The weight percent of P, G and A mixed with cellulose is given after the corresponding symbol, e.g., CP10G10 means TOCNF with 10% of PVA and 10% glyoxal. Reprinted with permission from Özkan, M., Karakoç, A., Borghei, M., *et al.*, 2019. Machine learning assisted design of tailor-made nanocellulose films: a combination of experimental and computational studies. *Polymer Composites* 40, 4013–4022.

considered as optimal designs since they are constantly evolving for multiple functions beyond carrying external loading. In their work, [Chen and Gu \(2019\)](#) designed superior composites from constituent materials by combining finite elements, molecular dynamics and machine learning (i.e., linear and nonlinear models, and CNN). Specifically, authors used graphene to create a novel nanocomposite with the topology predicted by machine learning. The CNN architecture trained and tested on 800 and 200K samples, respectively, provided the highest performance (MSE = 0.0002). In addition, the toughening and strengthening mechanism observed in composites at the continuum-scale by combining stiff and soft constituents seemed to be valid for nanomaterials as well.

Conclusion and Outlook

Smart cellulose materials couple the "smartness" functionality of smart materials with the unique attributes of cellulose – it is biobased, renewable, biodegradable, recyclable, carbon capturing and safe for humans and environment –. It is thus one of the most valuable assets of the circular economy. Current applications of cellulose extend much beyond its traditional use in the paper industry. Recent advances and applications of stimuli-responsive cellulose (nano)materials have been summarized by a large number of excellent reviews. Here, we aimed to grasp current research in the field of smart composite cellulose-based materials in shape-memory, wearable technology, and food packaging applications. In these applications, cellulose is often not merely a support medium but rather endows the final material or device with a useful, smart property. Examples of biologically inspired cellulose materials like the so-called electro-active papers (EAPaps) will likely appear in the forthcoming years. In parallel, the incursion of machine learning into materials science will accelerate the discovery of new materials and device designs. More powerful and advanced deep learning methods will be gradually adopted by the materials science community and cellulose composites will not escape from this anticipated revolution.

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Introduction: Processing of Composite Materials and Physical Characteristics

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Metal Matrix Composites

There are a wide variety of materials and routes for the production of composite materials ([Das and Das, 2021](#)). Metal Matrix Composites find high end applications the automotive, aerospace and energy sectors. Various casting routes for producing MMCs are presented in the article from [Palanivel et al. \(2021\)](#). These included stir casting, slurry casting, centrifugal casting, and squeeze casting. The basic technique, appropriate process parameters, advantages, and disadvantages of these techniques are presented.

It is presented in this article that until recently CNTs were the dominant carbon nano fillers used in metal matrix composites (MMCs) with extensive research work demonstrating that CNTs can provide a high degree of reinforcement of both mechanical and functional properties. The most significant requirements of MMC fabrication utilizing CNT include matrix reinforcement, interfacial reaction and chemical stability of the reinforcement. MMCs nowadays utilize advanced reinforcements including Carbon Nano Tubes (CNT), graphene and nano ceramic particles due to the potential delivering exceptional mechanical and other physical properties which offer enormous potential for a wide range of applications.

In a related article, [Ajithkumar and Xavier, 2021](#) present processing methods and properties resulting from CNT reinforcement of aluminum alloys. In this article, the effect of compaction, sintering, weight fraction, particle size and shape on final composite properties are noted. The formation of Al₄C₃ precipitates when processing above 500°C, was discussed. The formation of small amount of Al₄C₃ is reported as helpful in load transfer to CNTs by pinning the CNT to the matrix which provides increased strength in the composite. Larger amount of carbide or where carbide is not sufficiently formed can result in significantly reduced mechanical properties. Thermal degradation of the CNT can also lead to a decrease in mechanical properties. Good process and quality control are therefore required.

The powder compaction production route is an important route for composite material production. In the article Chaira, the implementation of this route for metal matrix composites is presented ([Chaira, 2021](#)). Powder production, additions, mixing, compaction and sintering processes are described. In the sintering section, conventional pressure-less, uniaxial and hot isostatic pressing, spark plasma sintering, and microwave sintering are presented. In addition to conventional die compaction, powder rolling, extrusion and dynamic compaction production routes are also presented. In the latter, rapidly solidified non-equilibrium structure is generated after consolidation. It is noted how pressure-less conventional sintering is a simple, low cost process which however consumes more time and achieves less densification as compared to uniaxial hot pressing/HIP and microwave sintering are complex processes. SPS is best suited for consolidation of nanoparticle/ultrafine particle, where nanostructure can be retained after consolidation with full density.

The development of sustainable and environmentally friendly production processes and materials is a critically important area of investigation in the coming years. In the section presented by Heidarzadeh *et al.*, recent developments in the green production routes and materials for metal matrix composite production are presented ([Heidarzadeh et al., 2021a](#)). In this article, the use of industrial and agricultural waste materials for this purpose are presented. The process route and resulting microstructures and mechanical properties of aluminum matrix composites reinforced with fly ash, snail shells, and egg shells are presented. The fabrication of green magnesium-cenosphere composites are presented in detail. Hollow spherical particles called fly ash cenosphere particles are naturally formed during the thermochemical process of coal-fired combustion in coal-fired power plants. The cenosphere particle which consist mainly SiO₂ and Al₂O₃ and have very low density, are strong, very low cost cheap and widely available. Alumina exhibits very good bonding with the magnesium matrix and improves the overall mechanical properties. These emerging composites present very good properties and great potential for the more sustainable development of metal matrix composites. The solid state production route for metal matrix composite production are also described ([Heidarzadeh et al., 2021b](#)).

These routes include powder metallurgy, diffusion bonding, forging (cold, warm and hot), Accumulative Roll Bonding (ARB), extrusion, explosive bonding, and Friction Stir Processing (FSP). These solid-state methods typically deliver superior microstructure and mechanical properties compared to those achieved from liquid processing routes. For each of these processes, to obtain improved properties, it is very important to optimize and control the process parameters for the selected base materials and reinforcements.

Further areas that are discussed within this section of the Encyclopedia include composite bonding, surface engineering, foam production, and in-situ reinforcement production techniques. The latter including exothermic dispersion, self-propagation high temperature synthesis, mechanical alloying, and additive manufacturing ([Keshavamurthy et al., 2021a](#)).

Polymer Matrix Composites

Materials used for matrix and reinforcement are described in the article by Kasiri and Brabazon ([Kasiri and Brabazon, 2021](#)). Nylon 6 was the first polymer used by Toyota in 1990 to make nanocomposites, whereas today thermoset polymers such as epoxy,

polyimide and thermoplastic polymers such as polypropylene, polystyrene are used as the matrix material of this composite. Nanomaterials reinforcements, between 1 and 100 nm, include fullerene, quantum dots (such as CdSe, CdS, etc.), carbon nanotubes, graphene/graphene oxides, diamond, and nanoclusters. Compared to traditional manufacturing technologies, additive manufacturing offers many exclusive advantages in terms of material efficiency, a straight-forward operating style, and better design flexibility. The development of polymer composites by additive manufacturing is presented further in the article by [Keshavamurthy et al. \(2021b\)](#).

The wide range of technologies that are used for polymer additive manufacturing are presented including material jetting, extrusion, binder jetting lamination, polymerization, and powder fusion. The inputs, outputs, opportunities and challenges for these processes are presented. These include the reduction of void formation, improvements in production time, improvements in mechanical properties, and enabling biocompatibility for biomedical implant applications. Case studies from the automotive and aerospace industries are presented.

As noted in the article from Singh and Sandhu, Acrylonitrile-Butadiene-Styrene (ABS) matrix based polymer composites provide very capable functional materials ([Singh and Sandhu, 2021](#)).

The good thermal, electrical, chemical, and mechanical properties of such composites are discussed. Their potential for functional polymer production and use in sensors is discussed. In this article, the effect of varying the composition of graphene on the resulting porosity, hardness and heat capacity are presented.

Ceramic Matrix Composites

Ceramic Matrix Composites (CMCs) are presented in a number of articles. Some specific examples are highlighted here. CMCs can be found in functionally graded thermal barrier coatings. The production of Functionally Graded Material (FGM) composite materials is presented by [Das et al. \(2021a\)](#).

FGM composites were originally developed for application in thermal barrier coatings. Surfaces developed with FGM coatings are used now in mineral processing and other industries where high wear resistance is required. Such composite FGMs as thin film coatings enable reduction of surface stress, peeling and microcrack formation. Methods used for producing FGMs are presented in this article as Physical Vapor Deposition, Chemical Vapor Deposition, Powder Metallurgy, centrifugal casting, tape casting, and solid freeform fabrication. The additive manufacturing techniques for FGMs of Laser-Powder Bed Fusion (L-PBF) and Laser Material Deposition (LMD) are presented. Friction stir processing, as well as centrifugal mixed powder and sintered casting methods are also discussed.

The used of composite materials in sensors and actuators are discussed in the article from [Das et al. \(2021b\)](#).

In this article, the sensing of load and electromagnetic sensing in radar systems are presented. Sensors materials examined included piezoelectric, optical, and resistive based materials. Actuators based on piezoelectric, ionic polymer metal composites, and electrorheological fluids were discussed; while the manufacturing methods of fiber and tape layup and bonding, filament winding and extrusion were presented.

New and Emerging Composite Material Technologies

The usage of a greater variety of materials and resultant increased production and produced device complexity are evident in the most recent developments in composite material production. This is highlighted in the article on multi-material production of 4D shape memory polymers from [Nyabadza et al. \(2021\)](#).

4D printing involves a material that can be transformed after 3D printing upon exposure to an external stimulus. The 4th dimension in 4D printing is time. It is expected that these emerging composite technology of Shape Memory Polymers (SMPs) as well as shape memory metals will have a major influence in the global economy and society in the next decade. The main production of metal matrix composites via metal additive manufacturing is presented in the article from [Mostafaei et al. \(2021\)](#).

Some specific examples of metal matrix composites produced in this manner are highlighted including aluminum, nickel, stainless steel metal matrix composites; as well as titanium, tungsten, and tungsten carbide ceramic metal matrix composites. Some challenges and opportunities of MMCs fabrication using the AM processes were highlighted including topology optimization, new AM equipment for composite production, process parameter optimization, and real-time process control. A further example of composite materials design is presented for the automotive industry in the article from [Kumar and Xavier \(2021\)](#).

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Processing Methods and Property Evaluation of CNT Based Metal Matrix Nano-Composites

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Introduction

Metal matrix composites (MMCs) are being presently used for a number of applications in aerospace, defense, and automobile industries because of its basic properties such as low density, high specific strength, high specific stiffness, and low expansion coefficient (Poovazhagan *et al.*, 2013; Kwon *et al.*, 2014; Jiang and Wang, 2015; Su *et al.*, 2012; Chandra Shekar *et al.*, 2014; George *et al.*, 2005; Pramanik *et al.*, 2008). Poor ductility and low fracture toughness reduces the applications of conventional composites in the above specified fields. To modify the ductility and fracture toughness of the conventional MMCs, the new class of materials called metal matrix nano composites (MMNCs) is developed through the use of nanoscale reinforcing particles (Poovazhagan *et al.*, 2013). MMNC have a greater potential compared to conventional MMC for usage in the same application areas, mostly structural, where a lower weight leads to reduce the energy requirement due to their advanced basic properties such as high specific strength, high thermal conductivity, excellent wear resistance, and controllable coefficient of thermal expansion (Bakshi and Agarwal, 2011). The number of research works related to metal matrix reinforced with carbon nanotubes (CNTs) has increased considerably, in last decade. This is mainly due to the attractive properties of these nano composites and the potential reinforcement offered by CNTs (Simões *et al.*, 2015). Commonly used nano carbon reinforcement materials are carbon nanotubes (CNTs) and carbon nano fibers (CNFs) (Hu *et al.*, 2013). In the above intimated particulate reinforced composites, more attention is observed for those reinforced with hard ceramic particles, due to the flexibility of controlling their mechanical properties by modifying the volume fraction, size and distribution of the reinforcements in the matrix. In the manufacturing of aluminum matrix composites, powder metallurgy (PM) technique is one of the favored routes and most widely used processing methods, due to its low production costs coupled with its high adaptability (Tabandeh Khorshid *et al.*, 2010; Esawi *et al.*, 2010). However, less research has been carried out in preparation, physical, and mechanical properties of metal–CNT nanocomposites. Similar to the conventional composites, the arrangement of the CNTs, uniformity in distribution of the composite, matrix adhesion, aspect ratio, and the volume fraction are the major contributors on the properties of the nanocomposite. Manufacturing based on these factors to obtain superior composites is challenging (Esawi *et al.*, 2009).

Matrix

A lot of metallic matrices have been examined to date; however, aluminum, titanium, copper, and magnesium are the most widely analyzed due to their higher strength to weight ratio compared to all the other structural metals (Poovazhagan *et al.*, 2013; Kwon *et al.*, 2014; Jiang and Wang, 2015; Su *et al.*, 2012; Bakshi and Agarwal, 2011; Simões *et al.*, 2015; Tabandeh Khorshid *et al.*, 2010; Esawi *et al.*, 2010; Esawi *et al.*, 2009; Lim *et al.*, 2012; Sasimurugan and Palanikumar, 2011; Uddin *et al.*, 2010; Lu *et al.*, 2013; Bastwros *et al.*, 2013; Liao and Tan, 2011; Kwon *et al.*, 2010; So *et al.*, 2013; Al-Qutub *et al.*, 2013; Liu *et al.*, 2012; Tofigh *et al.*, 2013; Thakur *et al.*, 2007; Baradeswaran and Elaya Perumal, 2014; Singhal *et al.*, 2013). Aluminum and magnesium have reserved their slot in the family of MMCs due to low density. Among these, magnesium has been found to have improved damping resistance, electromagnetic interference shielding, and manufacturability (Thakur *et al.*, 2007). Recently, Al–Si alloys are used widely in the automobiles for engine components such as cylinder blocks, cylinder heads, pistons, intake manifolds, piston rings, and different brackets. These Al–Si based alloys comprise approximately 85% of aluminum castings. These alloys were found to be a perfect substitute for cast iron components in most of the cases. Silicon can be added to aluminum without affecting the advantage of its lower weight because of its lower density compared to aluminum. Elements like silicon, zinc, magnesium, and copper have adequate solubility which makes them viable to be used as major alloying elements (Lu *et al.*, 2013; Tofigh *et al.*, 2013).

CNT

Carbon nanotubes (CNTs) have been capable reinforcements for nano composites, due to the superior mechanical, physical, chemical stability, high thermal conductivity, good electrical conductivity, high strength-to-weight ratio, high aspect ratio, and improved flexibility (Kwon *et al.*, 2014; Liao and Tan, 2011; Shimizu *et al.*, 2008; Hussain *et al.*, 2013; Mageswari *et al.*, 2014). As one of the unique nanomaterials, carbon nanotubes (CNT) have been the center of attention in terms of fundamental properties (Ruoff *et al.*, 2003). Addition of nanoscale SiC and CNT reinforcements reduce the coefficient of thermal expansion of Al and improve its yield strength & UTS and diminish failure strain. When we roll a sheet of carbon atoms, the carbon nanotubes will develop with a diameter of 1–2 nm which is known as single-walled carbon nanotubes (SWCNT). There are other types of carbon

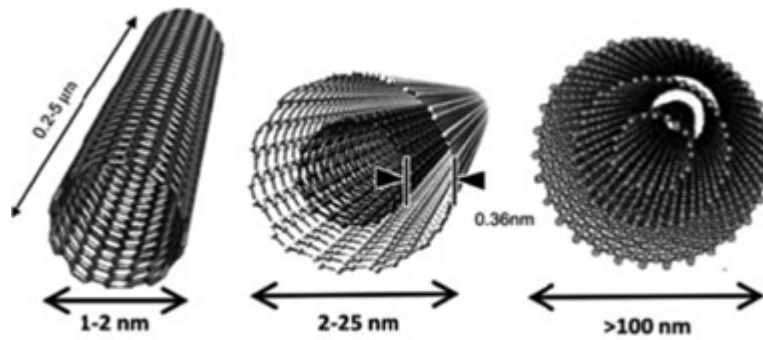


Fig. 1 Single, double, and multi-walled CNTs. Reproduced from Moghadam, A.D., Omrani, E., Menezes, P.L., Rohatgi, P.K., 2015. Mechanical and tribological properties of self-lubricating metal matrix nanocomposites reinforced by carbonnanotubes (CNTs) and graphene: A review. Compos. Part B Eng. 77, 402–420.

nanotubes which are double- and multi-walled with diameters ranging from 4 to 20 nm shown in [Fig. 1](#) ([Moghadam et al., 2015](#); [Bakshi et al., 2009a](#)). Single- and multi-walled carbon nanotubes have created considerable interest as strengthening materials for metallic, ceramic, and polymer composites because of their superior strength and stiffness ([Bakshi and Agarwal, 2011](#)). It is used to enhance the physical and mechanical properties of polymer, metal, and ceramic composites. The composite property is heavily dependent on the dispersion, length, crystal structure, and orientation of the CNTs, as well as the interface bonding between the CNT surface and base matrix. [Kwon et al. \(2010\)](#) reported that a 300% increase in tensile strength was achieved by the addition of 1 vol% CNTs to the Al matrix without any further treatment. Increasing CNT volume fraction reduces the density of the composites which could partly be due to the presence of porosities and voids ([Uddin et al., 2010](#)). SWNTs have greater mechanical properties, but still, they are not extensively used as reinforcement because they are highly expensive for the production and purification when compared with the MWNTs. One of the drawbacks of using MWNTs is that the tensile stresses can lead to the tearing off of the inner layer from the outer layers. This is known as telescoping effect/telescopic extension.

Mechanical Properties of CNT

Most of the measurement of the mechanical properties has been obtained through unconventional testing methods using small samples. Hence, it is difficult to develop an efficient correlation between processing methods, CNT dispersion, and mechanical properties of metal matrix/CNT composites. At present, there is only limited literature available about the elastic modulus due to higher attention on improving the yield/tensile strength. Processing methods adopted for the consolidation of the nano size powders into end product have a huge influence on its properties ([Bakshi and Agarwal, 2011](#)). [Ruoff et al. \(2003\)](#) have reported that the evaluated specific tensile strength of a single layer of an MWCNT can be as high as 100 times that of steel. The compressive strength of 100–150 GPa and compressive strain of 5% were reported. The covalent bond in the CNT contributes an important role in the improved mechanical properties of CNTs. It is observed that Young's modulus of 2.8–3.6 TPa, for SWCNT and 1.7–2.4 TPa for MWCNT ([Ruoff et al., 2003](#)). Recent research papers in this area have provided the elastic modulus of multi-wall carbon nanotube (CNT) to be between 600 and 1100 GPa, and the tensile strength was found to be between 35 and 110 GPa ([George et al., 2005](#); [Singhal et al. 2013](#)).

Powder Metallurgy

The manufacture of metal composites reinforced with CNTs is far behind when compared with polymer and ceramic matrix composites due to difficulties like as dispersion of CNT, mass production of extremely oriented CNTs, and boundary strength ([Kwon et al., 2010](#)). Several methods are available to produce particle reinforced MMCs. They are (1) Powder metallurgy processing (solid state), (2) Liquid state processing (melt/cast) and (3) Vapor deposition techniques (thermal spraying). (4) Electrochemical processing and (5) other novel techniques ([Bakshi and Agarwal, 2011](#); [Esawi et al., 2010](#); [Rajmohan and Kathirvel, 2012](#); [Bodunrin et al., 2015](#); [Bakshi et al., 2009b](#); [Baradeswaran and Elaya Perumal, 2013](#)). In the liquid state processing, the nano level reinforcement particles are mechanically well dispersed over the molten metal before the casting and solidification process. The most commonly used methods are stir casting, solid–liquid mixed casting and squeeze casting. Powder metallurgy (PM) is the most common solid state processing route due to availability of raw powder at cheaper cost and in good quality. In this processing powder blending, compaction and sintering are in the solid state and it can be a more attractive route if sintering can be faster, inexpensive, cleaner, low porosity, and flaws in the end product. Many methods have been experimented before for the production of MMCs over powder metallurgy route ([Chen et al., 2015](#)). However, microwave sintering has showed to be a process satisfying all the above mentioned requirements of inexpensive, lower lead time, and eco-friendly procedure ([Simões et al., 2015](#); [Esawi et al., 2009](#); [Thakur et al., 2007](#)). Recent years, powder metallurgy route has been generally used to develop the CNT/metal composites due to it's easier to integrate the CNTs into the metal matrix than casting and it can produce effective distributed CNT reinforced

metal matrix composites. However, it has certain limitations to produce in large product and is more expensive than the liquid state process. [Thakur et al. \(2007\)](#) reported that the magnesium-based hybrid nanocomposites with nano-sized silicon carbide and CNT reinforcements with very low porosity were effectively fabricated by powder metallurgy route via microwave sintering and hot extrusion. [Uddin et al. \(2010\)](#) CNT reinforced copper and copper alloy (bronze) composites have been fabricated via powder metallurgy route by hot press sintering. Hot extrusion has been favored as the last processing step due to the capability to produce high density composites ([Alizadeh et al., 2011](#); [Unlu, 2008](#)).

CNT Dispersion

The homogeneous dispersion of CNTs and wetting between the CNT and the metal has been among the main concerns in the manufacturing ([Bastwros et al., 2014](#)). Microstructural analysis confirms clusters of carbon nanotubes (CNTs) mainly at the grain boundary but also CNTs well dispersed and implanted in the aluminum matrix. Most of the research works have applied ball milling for enhancement of CNT dispersion and addition of CNTs to Al powders. [Esawi et al. \(2009\)](#) have attained good dispersion of 2 wt% CNTs in Al matrix by ball milling for 48 h at 200 rpm with a ball to powder ratio of 10:1. The studies show that in high energy ball milling, range of stiffening diminishes beyond 4–5 vol% due to comparatively poor dispersion. It is also reported that the CNT dispersion directly depends on the processing of powder and consolidation techniques. It was recommended to add reinforcements slowly to obtain better dispersion. The ultrasonication technique is one of the methods for dispersion of the CNTs in a molten metal by ultrasound energy. It is a very effective method for manufacturing untangled CNTs dispersed in liquids, such as water, acetone, ethanol or acids. The significance of ultrasonication duration on the structure of the CNT is shown in [Fig. 2](#).

The competence of this dispersion method depends on the liquid, ultrasound energy, time, and type of CNTs, a vital factor being the time essential for dispersion since longer time leads to their damage. A robust strengthening effect of the CNTs on the aluminum matrix was reported for the nanocomposites formed with 15 min of dispersion/mixture time. For shorter dispersion times than 15 min in ultrasonication, the dispersion will not be proper, which can lead to a reinforcement of the aluminum matrix, whereas high dispersion/mixture times creates a reduction in mechanical strength due to the damage caused by the increase in the number of defects and junctions or boundaries of CNTs ([Simões et al., 2015](#)). However, high energy ball milling is recommended for better CNT dispersion for CNT based metal matrix composite.

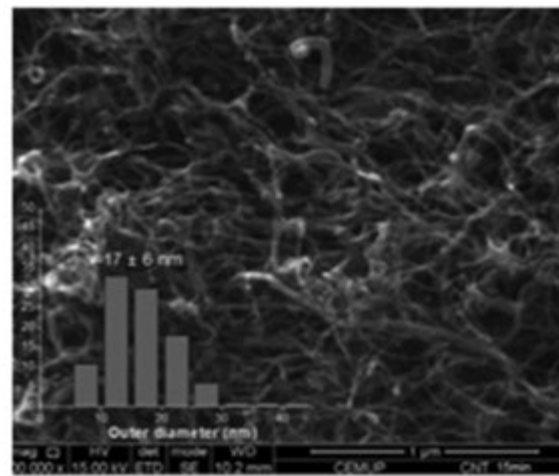
High Energy Ball Milling

High energy ball milling is one of the effective tools for mixing as well as grinding. A large amount of energy is involved in the ball milling because the dispersion is obtained by collisions of dense and rigid balls with the CNTs, which comprise of repeated cold welding, fracturing, and re-welding of powder particles in a high-energy ball mill ([Kwon et al., 2012](#)). The milling jars were filled with an inert gas like argon to protect powders from the atmospheric reaction. Methanol/nitric acid/stearic acid/heptane were the commonly used process control agent (PCA) to reduce cold welding of metal powders. It also helps to prevent sticking to the balls and the jar walls. It is used to achieve a homogenous distribution of the reinforcement in metal matrix nano composites, thereby diminishing the chances of agglomeration ([Bastwros et al., 2014](#); [Kwon et al., 2012](#); [Esawi and Morsi, 2007](#); [Prashanthakumar and Anthony Xavier, 2016](#)). It was concluded that the proper selection of process control agent has a significant outcome on the powder morphology and the hardness. Heptane improves the welding ability of the powders during milling ([Al-Qutub et al., 2013](#)). Pre-treatment of CNTs, type of milling, ball-to-powder (BPR) weight ratio, speed of milling, milling time, and process control agent are the deciding factors of dispersion of CNT in metal matrix nano composite ([Kwon et al., 2012](#)). Milling speed and amount of balls are the most significant factors to decide the final size of the particles in planetary ball milling ([Mierczak et al., 2015](#)). [Bastwros et al. \(2013\)](#) identified that low BPR could reduce the possible damage to the CNTs. CNTs can implant into the soft and ductile matrix through the solid diffusion techniques due to the high impact energy. How the CNTs implanted between the re-welded particles are shown in [Fig. 3](#). It has been addressed that, the increasing milling time, the CNTs will gradually lose its tubular structure, and more than 50 h of milling, the tubular structure would completely vanish.

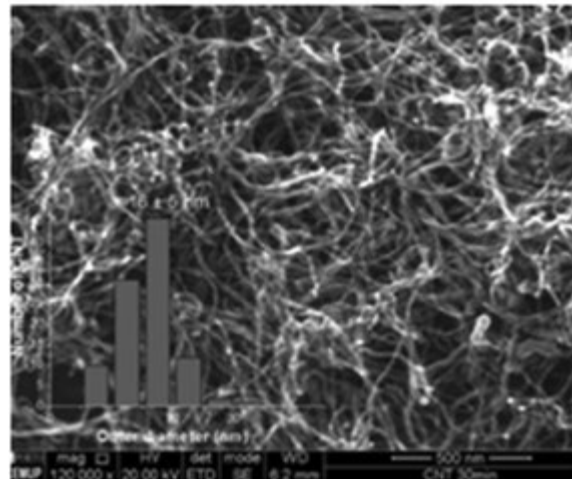
The hardness of the powders normally increases with the increase in milling time and the speed of milling. The milling speed has a more influencing factor when the milling is achieved with smaller balls. For higher milling speeds, the smaller ball size appears to be additional advantageous and lead to increase the hardness values. Optimization of milling process variables becomes essential for obtaining the better results ([Esawi et al., 2009](#); [Singhal et al., 2013](#)).

Effect of Milling Time

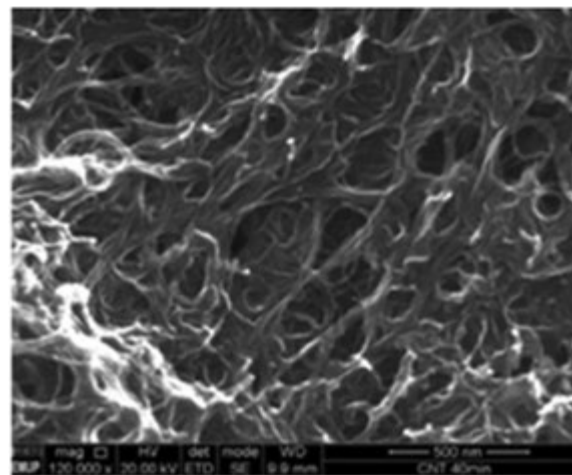
The milling time having a significant influence in the shape and micro structure of the Al particles in the composite powders and also changed concerning the milling time. In SiC and CNT based hybrid composites, the SiC interface layer on the CNT surface can be successfully created by a three-step process: (1) mechanical crushing, (2) coating of crushed Si nanoparticles onto CNT surfaces, and (3) formation of a SiC layer by high-temperature annealing treatment ([So et al., 2013](#)).



[a]



[b]



[c]

Fig. 2 SEM images showing the structure of the CNT and the outer diameter distributions of the CNT dispersed by ultrasonication for (a) 15, (b) 30, and (c) 40 min. Reproduced from Simões, S., Viana, F., Reis, M.A.L., Vieira, M.F., 2015. Influence of dispersion/mixture time on mechanical properties of Al-CNTs nanocomposites. *Compos. Struct.* 126, 114–122.

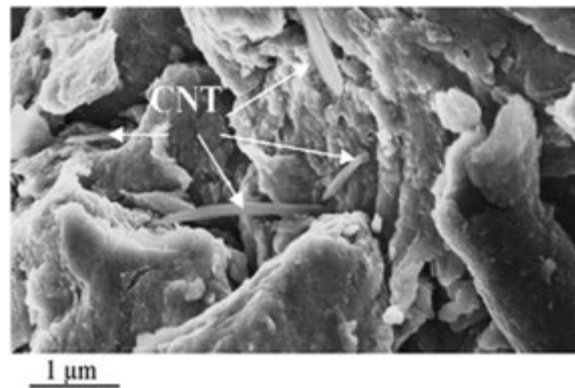


Fig. 3 CNTs implanted between the re-welded particles after 3 h of milling. Reproduced from Esawi, A.M.K., Morsi, K., Sayed, A., Abdel Gawad, A., Borah, P., 2009. Fabrication and properties of dispersed carbon nanotube–aluminium composites. *Mat. Sci. Eng. A Struct.* 508, 167–173.

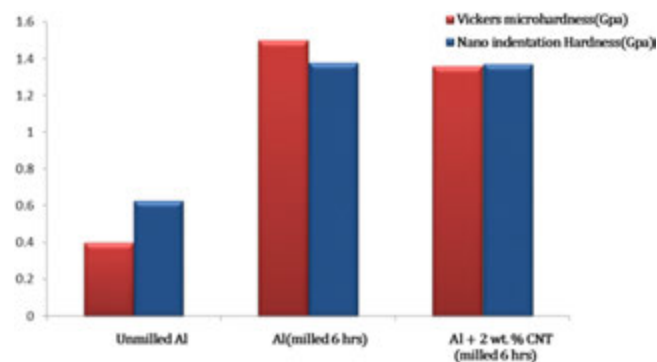


Fig. 4 Vickers micro-indentation and nano-indentation hardness of un-milled and milled pure Al and Al 2 wt% CNT extruded samples. Reproduced from Esawi, A.M.K., Morsi, K., Sayed, A., Abdel Gawad, A., Borah, P., 2009. Fabrication and properties of dispersed carbon nanotube–aluminium composites. *Mat. Sci. Eng. A Struct.* 508, 167–173.

The Vickers hardness and bending strength of the hybrid nano particle reinforced composites were improved with increasing milling time and exposed the highest values that were around five times more than that of pure Al6061 alloy. **Fig. 4** shows the relationship between milling time and hardness of un-milled and milled (6 h) pure Al and Al 2 wt% CNT extruded samples.

Milling time between 60 and 120 min exhibited the most improvement in the mechanical properties, because of particle shape and size effects. The effect of milling on the hardness of the Al/SiC 1 vol% composite is shown in **Fig. 5**. Hence, the milling time between 60 and 120 min and speed between 250 and 450 rpm recommended for planetary ball milling of CNT based metal matrix nano composites.

Sintering

After ball milling, powders will be compacted in a die using a uniaxial press with adequate pressure. Based on the literature 300–570 MPa pressure recommended for CNT based metal matrix composites (Esawi *et al.*, 2010; Esawi *et al.*, 2009; Al-Qutub *et al.*, 2013). The relative density of the compacts mainly depends on the pressure applied and holding time (Ardestani *et al.*, 2014). Holding time played a significant role for the cold welding effect during compaction. After the cold compaction microwave sintering was used by most of the researchers. The optimization of sintering parameters such as temperature, time, heating, and cooling rate are required for every composite (Uddin *et al.*, 2010). The parameters such as holding time, ramp rate, pulse duration, pulse current, and voltage are used to control of sintering temperature.

Al-Qutub *et al.* (2013) reported that the microstructure of Al6061 with 1 wt% CNT sintered at the temperature of 400°C for 20 min exhibited only very small pores were present, and the further increase of sintering temperature to 450°C leads to the densification of the matrix. How the pores are decreasing is indicated in **Fig. 6**. Similarly, the hardness of the matrix increased from 57 to 66 HV with the further increase the sintering temperature of 50°C. Hence, they concluded that higher sintering temperature increases the rate of diffusion and reduces the porosity. So the density and hardness of the composite increased significantly. Spark plasma sintering (SPS) is another sintering method which is suitable for the densification of unsinterable materials and creation of sound interface bonding (Kwon *et al.*, 2010). The sintering temperature ranges from 500 to 650°C suitable for Al–CNT based metal matrix composites.

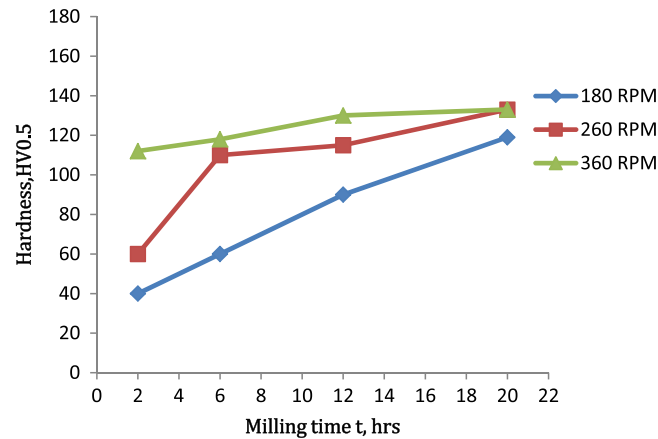


Fig. 5 The hardness of compressed samples vs. milling time (20 mm balls). Reproduced from Al-Qutub, A.M., Khalil, A., Saheb, N., 2013. Wear and friction behavior of Al6061 alloy reinforced with carbon nanotubes. *Wear* 297, 752–761.

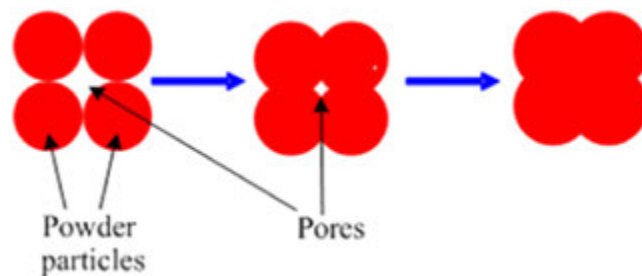


Fig. 6 Shows the principle of the sintering process.

Hot Extrusion

Hot extrusion increases the density of the composite at the final stage and creates fine microstructure. The hydraulic or mechanical ram gives the pressure on the sintered billet through a die to make a product into a required shape (Tabandeh Khorshid *et al.*, 2010; Tokutomi *et al.*, 2015). Cold compaction and hot extrusion process are suitable for consolidating the ball milled Al–CNT/Mg–CNT composite (Bastwros *et al.*, 2013; Tokutomi *et al.*, 2015; Goha *et al.*, 2006; Deng *et al.*, 2007). The extrusion ratio and temperature of extrusion are the most influencing factors in this process. Colloidal graphite mostly used as a lubricant for the hot-extrusion process (Thakur *et al.*, 2007). To reduce the notch sensitivity and improve the ductility, extruded samples must be annealed with required pressure and temperature. Extrusion was also initiated to promote alignment of CNTs in the direction same as that of extrusion, and they reported after the extrusion with the temperature of 500°C and annealing process slight growth in mean crystal size took place (Esawi *et al.*, 2009). Higher extrusion ratio and higher pressure during hot pressing are estimated to yield better improvements. Large extrusion ratio indicates higher degree of deformation, which leads the alignment of CNTs along the direction of extrusion as well as the breakdown of CNT clusters (Bakshi and Agarwal, 2011).

Effect of Reinforcements

Reinforcing the ductile matrix with tougher and hard reinforcements like oxides, carbides, borides, and nitrides offers an integrated property of the metallic matrix as well as ceramic reinforcement components, which will enhance the physical and mechanical properties of the composites (Tabandeh Khorshid *et al.*, 2010). Silicon carbide (SiC), aluminum oxide (Al₂O₃), and graphite are mostly used reinforcements in the form of particles or whiskers (Lu *et al.*, 2013; Baradeswaran and Elaya Perumal, 2014; Ahmad *et al.*, 2010). Limited experiments have been published on CNT reinforced matrix composites due to the higher cost of CNT and poor wettability with the matrix. However, CNT is an impressive reinforcement material because of its excellent chemical and thermal stability, anti-wear behavior and lubrication effects (Lu *et al.*, 2013). The effect of reinforcement materials and processing methods on the properties of the composite are listed in Table 1. The motivating factor behind the addition of ceramic reinforcements and CNTs into a metallic matrix can enhance specific strength, stiffness, friction and wear, fatigue and creep properties compared to conventional materials and alloys (Rabiei *et al.*, 2008).

Table 1 Effect of reinforcement materials and processing methods on the properties of composite

Matrix	Reinforcements	Processing methods	Properties	Ref
Al 6061	SiC (0.5, 1.0 and 1.5 vol%) + B ₄ C (fixed 0.5 vol%)	Ultrasonic cavitation	The addition of a lesser amount of nanoparticles enhances the tensile strength. The excellent tensile strength was attained at the hybrid ratio of 1.0 vol% of SiC and 0.5 vol% B ₄ C and after that, tensile strength decreased. The hardness of the composites enhances as the hybrid ratio increases.	(Poovazhagan <i>et al.</i> , 2013)
Cu alloy	MWCNT (0.1 wt%)	Hot-press sintering	The hardness of copper matrix composite has upgraded up to 47% compared to that of pure matrix, and the electrical conductivity of bronze composite has enhanced up to 20%.	(Uddin <i>et al.</i> , 2010)
Al	2 wt% MWCNT	Cold compaction and hot extrusion	Tensile strength improved to 21%.	(Esawi <i>et al.</i> , 2009)
Al6061	MWCNT + nSiC	High-energy ball milling and hot-pressing	The Vickers hardness and bending strength of the hybrid nanoparticulate composites were improved with increasing milling time about 5 times greater than those of pure Al6061alloy.	(Kwon <i>et al.</i> , 2014)
AZ31 Mg alloy	nAl ₂ O ₃ + CNT	Friction stir processing	The hybrid effect of (0.2% Al ₂ O ₃ 0.1% CNTs)/AZ31 composite has the maximum micro hardness about 1.4 times higher than those of AZ31 Mg alloy.	(Lu <i>et al.</i> , 2013)
Al	MWCNT	Cold compaction and hot extrusion	The wear rate of the 5% wt CNT composite reduced by approximately 78.8% compared to pure matrix.	(Jiang and Wang, 2015)
Al	0.5 wt% of CNTs	High-energy ball milling and polyester binder-assisted (PBA) approach	Minor addition of CNTs (0.5 wt%) considerably improved the strength and hardness of the composite. The PBA and high energy ball-milling were better compared to that of the low energy ball-milling.	(Liao and Tan, 2011)
Al	nAl ₂ O ₃	Wet attrition milling and hot forward extrusion	Increasing the weight fraction of the nanoparticles, the hardness and strength of the composites first improved and then reduced when the amount of the nanoparticle is more than 4 wt%.	(Tabandeh Khorshid <i>et al.</i> , 2010)
Al	1 vol% MWCNT	Spark plasma sintering followed by hot-extrusion	Presence of CNTs in the boundary layer has improved the mechanical properties.	(Kwon <i>et al.</i> , 2010)
Al	5 wt% MWCNT	Cold compaction and hot extrusion	Increase of up to 50% in tensile strength and 23% in stiffness compared to pure Al. Carbide formation was noted in the composite containing 5 wt% CNT.	(Esawi <i>et al.</i> , 2010)
A356.2	1 wt% MWCNT	Ball milling and Die casting	The tensile strength and Young's modulus improved by 15% and 79%, respectively, after the addition of 1 wt% CNTs.	(So <i>et al.</i> , 2013)
2009Al	CNT	Powder metallurgy and friction stir processing	Increasing the CNT fraction from 0 to 3 wt% lead to an increase in the YS. The UTS increased with increasing the CNT fraction from 0 to 1 wt% and it was decreased as the CNT fraction increased up to 3 wt%	(Liu <i>et al.</i> , 2012)
Al 7075	Al ₂ O ₃ + 5 wt% graphite	Stir casting	The hardness of hybrid composites improved with increasing Al ₂ O ₃ . Addition of Al ₂ O ₃ particle improved the tensile and compressive strength.	(Baradeswaran and Elaya Perumal, 2014)

Effect of Volume/Weight Fraction

The properties such as density, specific strength, stiffness, coefficient of thermal expansion, thermal conductivity, wear resistance, the weight of the end product, etc., are the function of volume fractions of reinforcements (Tsai and Lu, 2009; Kemal Apalak *et al.*, 2009). Relationship between CNT volume fraction and Brinell hardness of MWCNT/Al-Mg composites is shown in Fig. 7. That indicates the hardness of the composite increases with the addition of volume fraction up to a particular level, and further addition reduces the hardness. Tsai and Lu (2009) observed improvement in the tensile strength up to 50% compared to pure aluminum matrix with the addition of 2 wt% CNT and more than 5% addition of CNT did not contribute any additional improvements in the mechanical properties of the composite. Jiang and Wang (2015) reported that increase of SiC volume fraction from 0.5% to 1% led to an enhancement of yield strength about 17% and ultimate tensile strength about 7% and further addition decreases the same properties. The percentage of elongation reduced with the increasing volume fraction of SiC particles, and more than 5% volume fraction decrease in the strength of the composite was observed.

Effect of Particles Shape and Size

The shape and size of the matrix as well as reinforcement particles, choice of CNT (single-walled or multi-walled), etc., are important factors for influencing the mechanical and physical properties of the final composites. The dendritic shape of the metal

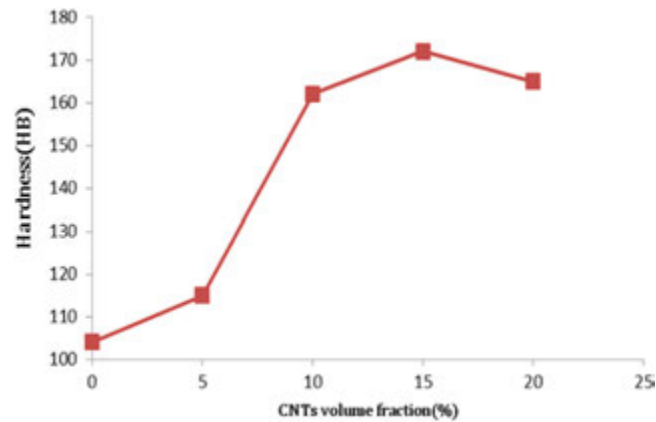


Fig. 7 Relationship between CNT volume fraction and Brinell hardness of MWCNT/Al-Mg composites under a functional load of 30 N and a sliding velocity of 1.57 m/s. Reproduced from Moghadam, A.D., Omrani, E., Menezes, P.L., Rohatgi, P.K., 2015. Mechanical and tribological properties of self-lubricating metal matrix nanocomposites reinforced by carbonnanotubes (CNTs) and graphene: A review. *Compos. Part B Eng.* 77, 402–420.

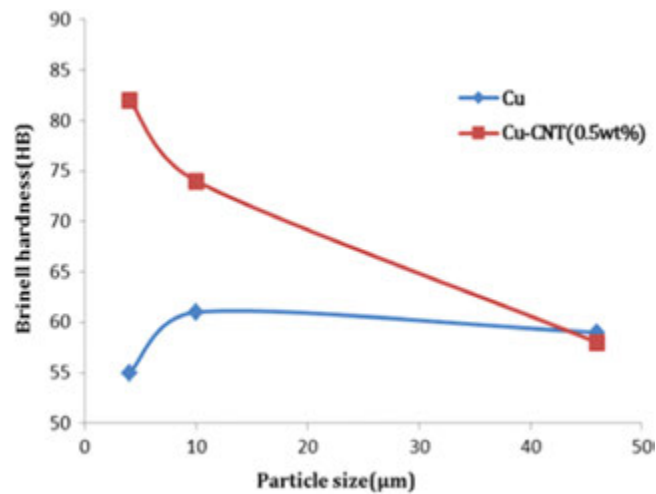


Fig. 8 The hardness of Cu/MWNT composites fabricated with different metal particles size. Reproduced from Uddin, S.M., Mahmud, T., Wolf, C., *et al.*, 2010. Effect of size and shape of metal particles to improve hardness and electrical properties of carbon nanotube reinforced copper and copper alloy composites. *Compos. Sci. Technol.* 70, 2253–2257.

or reinforcement particles has more specific surface area and it probable to improve CNT distribution (Uddin *et al.*, 2010; Thakur *et al.*, 2007). In high energy, ball milling results in strain hardening, which decreases the ductility leading to the reduction of particle size. Increase in the milling time leads to an increase in strain hardening, which results in more particles fracturing than re-welding, and refined particle size (Esawi *et al.*, 2009). Higher ball milling process time instigates an increase in the number of small diameter nanotubes.

From the graph provided in Fig. 8 we can identify that the hardness of pure copper is constant during the increase in particle size whereas in Cu–CNT hardness diminishes as the particle size is increased.

Load Transfer in CNT

The load transfer efficiency is the efficiency by which the surrounding matrix can transfer the load to the carbon nanotubes (CNTs) or reinforcements. The load transfer efficiency from the matrix to the CNTs is a key parameter for the mechanical property of the CNT based nano composites (Chen *et al.*, 2015). It was witnessed that the SWCNTs have a better load transfer efficiency than the MWCNTs, keeping the volume fraction same. The reduction in the load transfer efficiency can be related to the number of graphite layers in the MWCNT, and this can be enhanced by creating proper chemical bonding between the graphite layers (Zalamea *et al.*, 2007). Composites with a higher density are observed to have better CNT–matrix contact leading to better load transfer to CNTs. Extrusion can enhance the density viz. a large extrusion ratio can impart a higher degree of deformation. This, in turn, was observed to increase the extent of the orientation of CNTs along the direction of extrusion leading to disintegration of CNT

clusters; stronger bond resulting in a better load transfer (Bakshi and Agarwal, 2011). It was noted that the number of layers of CNT and the load transfer efficiency is inversely related. The chemical bonding between the walls can drastically enhance the load transfer from the outer layer to the inner layers. The load transfer efficiency to the MWCNTs was greater in compression and low in tension (Chen *et al.*, 2015). It was also reported that only the outermost layer was stressed in tension when tensile loads are applied, whereas all the layers multi wall carbon nano tube respond in compression (Tsai and Lu, 2009).

Formation of Al_4C_3

Most of the researchers reported the aluminum carbide formation in the nano composites (Simões *et al.*, 2015; Esawi *et al.*, 2009; So *et al.*, 2013; Kwon *et al.*, 2012; Lipecka *et al.*, 2011). The formation of Al_4C_3 occurs at a higher processing temperature of the composite mostly above 500°C , and it occurs during the sintering process (Simões *et al.*, 2015). More than 5% volume fraction of CNT creates severe carbide formation. The formation of Al_4C_3 at cross section and fracture surface of Al-10 wt% CNT is indicated in Fig. 9. Esawi *et al.* (2010) confirmed that the formation of Al_4C_3 in composite consisting of 5 wt% CNT at the temperature of 656°C and Al_4C_3 formation strongly dependence on the processing temperatures who examined various annealing temperatures ranges from 450 to 950°C (Esawi *et al.*, 2009; Bakshi *et al.*, 2009a; Lipecka *et al.*, 2011). The carbide layer may be thin or thick. Formation of traces of Al_4C_3 is helpful in load transfer to CNTs by pinning the CNT to the matrix. This also adds to the increase in the strength of the composite. Bakshi and Agarwal (2011) have observed a 57.5% enhancement in the tensile strength by addition of 2 wt% CNTs. He also reported that pure copper does not produce carbide, which reduces the chances of the chemical reaction between the two. These chemical reactions occurring between aluminum and CNT can cause thermal degradation which leads to the destruction of the CNT structure due to the formation of unstable phases creating a steep drop in the mechanical properties (Su *et al.*, 2012; Tsai and Lu, 2009). So *et al.* (2013) identified a possible solution for this problem viz. by decorating the surfaces of CNTs with nano-sized ceramic particles, for example, silicon carbide (SiC).

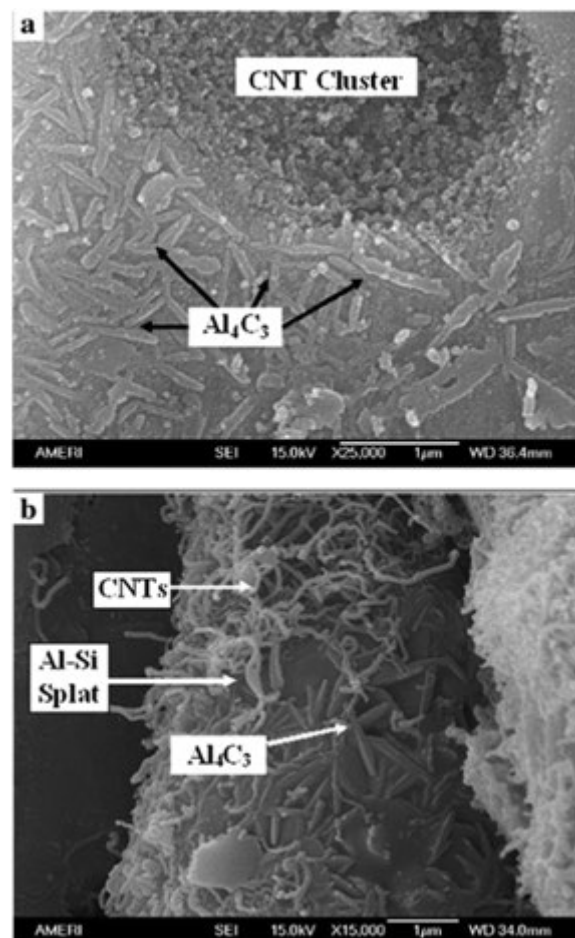


Fig. 9 SEM morphology showing Al_4C_3 formation in Al-10 wt% CNT (a) cross section and (b) fracture surface. Reproduced from Bakshi, S.R., Singh, V., Seal, S., Agarwal, A., 2009b. Aluminum composite reinforced with multiwalled carbon nanotubes from plasma spraying of spray dried powders. *Surf. Coat. Tech.* 203, 1544–1554.

Factors Affecting Strengthening

Dispersion of CNT in the powder stage, type of reinforcements, volume fraction, ball milling time, compaction pressure, deformation rate, sintering temperature, and the interface bonding between matrix and CNT are the major factors to influence the strength of the hybrid composite. However, CNT dispersion in the matrix is the major influencing parameter that has shown superior strengthening results. Effective strengthening and load transfer efficiency depend on the amount of deformation of the composite during fabrication, in which huge deformation processes show better strengthening effect (Lim *et al.*, 2012). Annealing is recommended after the extrusion for the enhancement of strength and ductility. Bakshi and Agarwal (2011) mentioned that volumes fraction ranges from 0% to 5% improve the efficiency of strengthening and reduces with increasing CNT content more than 5% (Bakshi and Agarwal, 2011). Lim *et al.* (2012) investigated that CNF dispersion increased the strength of the nanocomposites around 38% and proved that CNFs could be an impressive reinforcement for strength enhancement of pure aluminum matrix. Tabandeh Khorshid *et al.* (2010) have shown that the reduction in particle size is of equal importance to the increase in the volume of the nanoparticles, resulting to the enhancement in the strength. However, the amount of nanoparticles exceeds a particular level, they occupy the grain boundaries which lead to the formation of a continuous brittle phase on the grain boundaries, minimizing grain boundary pinning effect and reducing the strength of the composites (Tabandeh Khorshid *et al.*, 2010).

Mechanical and Thermal Properties

The composite mechanical property can be improved by controlling of cooling rate, the volume fraction, size, shape, spatial distribution of the reinforcement. How the externally applied load is transferred to the reinforcement materials is an important factor for finalizing the mechanical properties (Tofigh *et al.*, 2013). Micro hardness and the uniaxial tensile strength are the major determining factors for determining the mechanical properties of the composites (Tabandeh Khorshid *et al.*, 2010). If the size of the particles changed from microscale into nanoscale, the mechanical properties could enhance considerably (Maddahi *et al.*, 2014).

Hardness

Reinforcement particles types and its volume fractions are having a significant role in the hardness of the composite. Monolithic magnesium showed the least micro-hardness value when compared to the Mg/CNT based composite samples (Shimizu *et al.*, 2008). The combination of Mg added with 0.3% CNT and 0.7% SiC showed the maximum micro-hardness value, and micro hardness reduces with a decrease in the amount of SiC.

The addition of reinforcement to the Al matrix mostly improves the micro hardness of the composites, and it mainly depends on the type and volume fraction of reinforcements. It was noted from the literature that the micro hardness of the composites rises to almost 93 HV for the composites containing up to 4 wt% of CNT. Further increase in the weight percentage of CNT leads to a drop in the micro-hardness (Tabandeh Khorshid *et al.*, 2010). From Fig. 10, we can understand that the Brinell hardness values of the composites enhance with the addition of CNT up to a particular level in copper-based CNT composite. The addition of SiC and B₄C nanoparticles improve hardness, because they are harder than Al alloy, which provides hardness to the soft matrix. It can also be observed that the presence of stronger hybrid reinforcements in the Al matrix, effectively stop the development of dislocations which leads to the improvement in the hardness and strength of the hybrid composites (Poovazhagan *et al.*, 2013).

Fig. 11 indicates the increase in annealing time decreases the hardness values concerning the temperature. Ball milling also contributing to the hardness of the CNT based composites. It was clear that the hardness of the pure aluminum ball milled

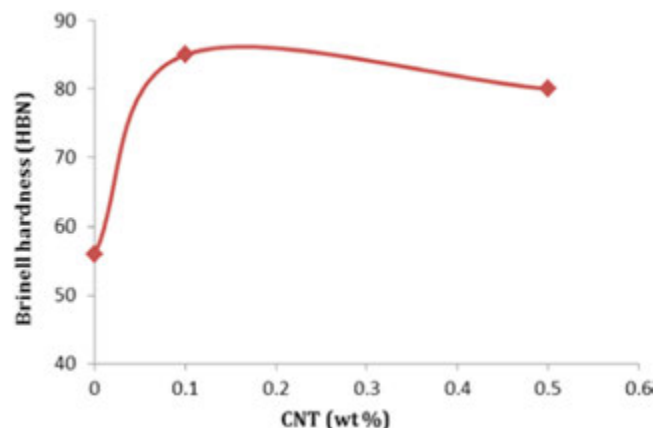


Fig. 10 Relationship between Brinell hardness and CNT wt% of Cu (3 μ m)/CNT composites. Reproduced from Uddin, S.M., Mahmud, T., Wolf, C., *et al.*, 2010. Effect of size and shape of metal particles to improve hardness and electrical properties of carbon nanotube reinforced copper and copper alloy composites. *Compos. Sci. Technol.* 70, 2253–2257.

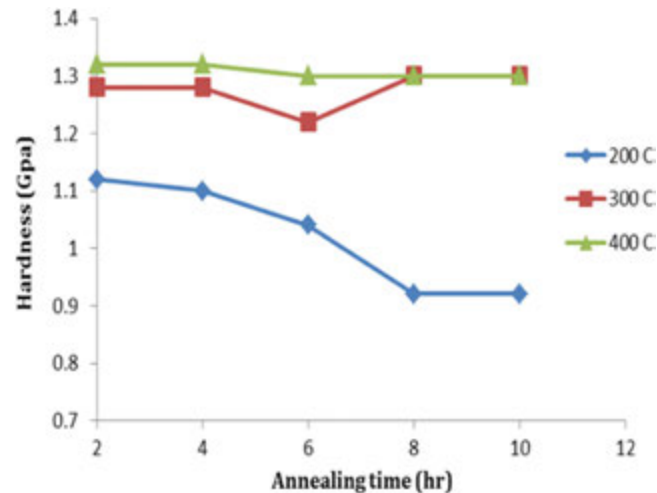


Fig. 11 Variations of Vickers hardness at the considered annealing temperatures and times for ball-milled pure aluminum matrix extrudates. Reproduced from Esawi, A.M.K., Morsi, K., Sayed, A., Abdel Gawad, A., Borah, P., 2009. Fabrication and properties of dispersed carbon nanotube–aluminium composites. *Mater. Sci. Eng. A Struct.* 508, 167–173.

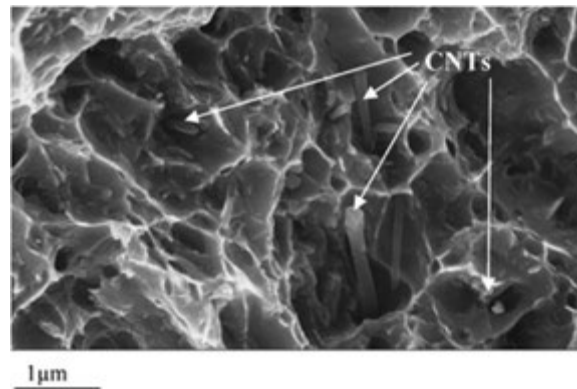


Fig. 12 Fracture surfaces of the tensile specimen of Al/2 wt% CNT at 6 h of ball milling (un-annealed). Reproduced from Esawi, A.M.K., Morsi, K., Sayed, A., Abdel Gawad, A., Borah, P., 2009. Fabrication and properties of dispersed carbon nanotube–aluminium composites. *Mater. Sci. Eng. A Struct.* 508, 167–173.

composite improved by 90% compared to the unmilled samples due to the strain-hardening effect of ball milling (Kwon *et al.*, 2014; Lu *et al.*, 2013). Esawi *et al.* (2010) observed that the addition of CNTs improved the hardness additionally to reach its extreme value of 95.2 HV for the Al 5 wt% CNT samples. It was reported that the hardness of the CNT reinforced composite increased due to the filling of CNTs in the micro-voids of the Al particles. However, adding carbon nanotubes to composite increases the hardness and an excessive increase in the quantity of CNT cause the hardness and stress to decrease, hence friction and wear increases (Kim *et al.*, 2009).

Tensile Strength and Yield Strength

The composite containing the alumina reinforcement particle reveals superior yield and tensile strengths compared to the pure aluminum matrix. The volume fraction of the reinforcement nanoparticles more than 4 wt%, the strengths of the composites start to decrease. It was observed that from the several studies, the strength of the composite improved by decreasing particulate size (Tabandeh Khorshid *et al.*, 2010; Goh *et al.*, 2008). Ball milled aluminum matrix was reported around three times higher tensile strengths compared with un-milled Al particles. The fracture surface of tensile specimens of Al/2 wt% CNT at 6 h of ball milling under un-annealed and annealed for 10 h at 500°C is shown in Figs. 12 and 13. The rate of improvement of elastic modulus reduced with increasing CNT volume fractions. Bakshi and Agarwal (2011) reported that after the significant addition of CNT ranges from 5 and 10 wt% decline in the tensile strength around 24%–25% of Al with 12 wt% Si alloy. The decline in the values is attributed to the existence of un-infiltrated or partially infiltrated CNT clusters. From Fig. 14, it can be noted that the tensile strength values of the hybrid composites are higher than that of the unreinforced counterpart and the combination 1% SiC and

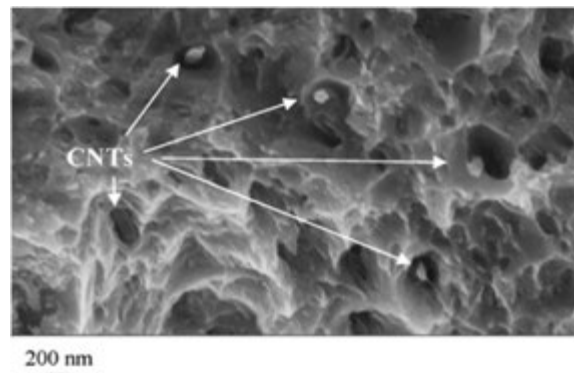


Fig. 13 Fracture surfaces of the tensile specimen of Al/2 wt% CNT examined at 6 h of ball-milling (annealed at 500°C for 10 h). Reproduced from Esawi, A.M.K., Morsi, K., Sayed, A., Abdel Gawad, A., Borah, P., 2009. Fabrication and properties of dispersed carbon nanotube–aluminium composites. *Mater. Sci. Eng. A Struct.* 508, 167–173.

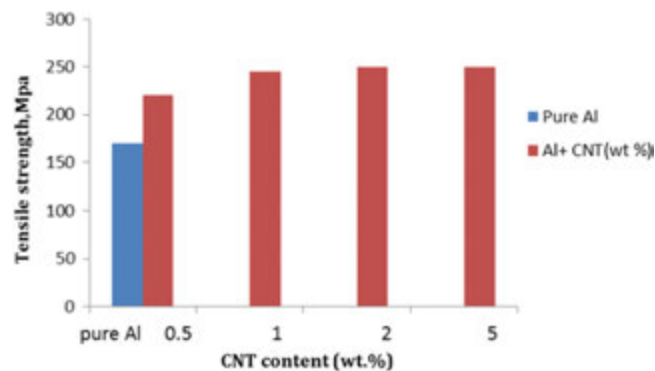


Fig. 14 Variations of the effect of CNT wt% on the tensile strengths of the examined pure Al and Al/CNT composites. Reproduced from Esawi, A. M.K., Morsi, K., Sayed, A., Lanka, S., 2010. Effect of carbon nanotube (CNT) content on the mechanical properties of CNT-reinforced aluminium composites. *Compos. Sci. Technol.* 70, 2237–2241.

0.5% B₄C give better tensile strength. The enhancement of the tensile strength was dedicated to the presence and homogenous distribution nano reinforcements. The in-built reinforcements create a barrier to dislocation movements of the particles. When the percentage of SiC increases above 1%, there is a drop in the tensile strength of the matrix.

The drop can be due to the increased agglomeration of the nanoparticles and increased porosity as the particle percentage increases. Agglomeration leads to the micro clusters and the slackly packed particles in the clusters making the material weaker and hence will lead to a reduction in tensile strength (Poovazhagan *et al.*, 2013). The yield of CNTs concerning the ratios of SiC/CNT composite also indicated in Fig. 15.

Compressive Strength

The ultimate compressive strength of the composite improved with increase in the presence of nano ceramic reinforcements and CNT. It was reported that the compressive strength reduced due to the addition of reinforcement like graphite (Baradeswaran and Elaya Perumal, 2014), and to improve the compressive strength reinforcement such as SiC, B₄C, and Al₂O₃ are recommended. Baradeswaran and Elaya Perumal (2014) observed that compressive strength of the hybrid nanocomposite was improved about 10% more than the base matrix with the addition of Al₂O₃. This is because of the hybrid nanocomposites became tougher with the increased amount of hard reinforcements particulate. Addition of graphite to aluminum matrix reduces not only the compression strength, but also the hardness, tensile strength, and flexural strength and it can be overcome by the addition of hard Al₂O₃ particles in the hybrid composites. So the graphite is not preferred for obtaining good compressive strength in CNT based metal matrix composites.

Young's Modulus

The percentage of elongation decreases progressively with increase in the volume fraction of nanoparticle due to the result of the effective mixing of nanoparticles. Porosity influences Young's modulus values (Su *et al.*, 2012). Tsai and Lu (2009) investigated

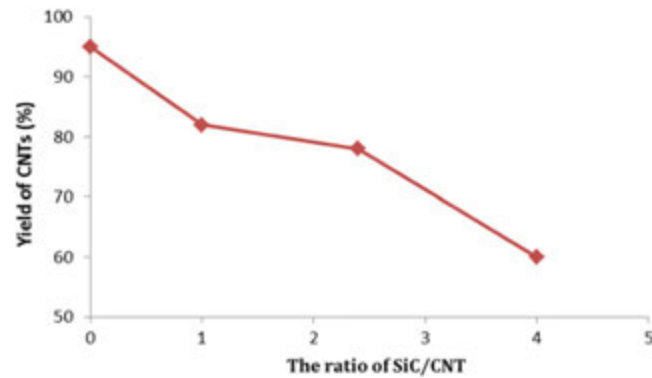


Fig. 15 Relationship between the ratios of SiC/CNT composite yield after annealing. Reproduced from So, K.P., Jeong, J.C., Park, J.G., *et al.*, 2013. SiC formation on carbon nanotube surface for improving wettability with aluminum. *Compos. Sci. Technol.* 74, 6–13.

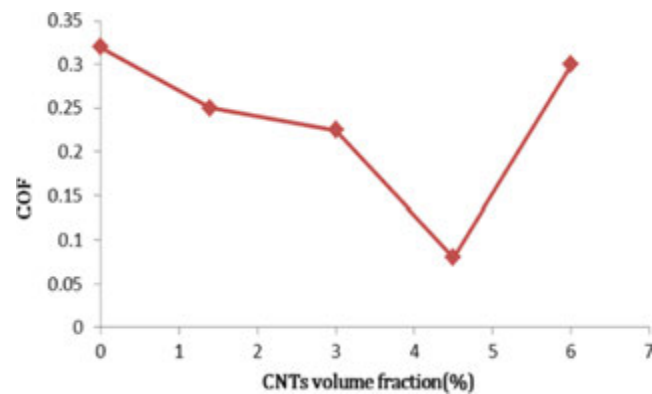


Fig. 16 Effect of volume fraction of CNT on the coefficient of friction Al/CNT nano composite under the load 30 N and sliding speed 0.12 m/s. Reproduced from Moghadam, A.D., Omrani, E., Menezes, P.L., Rohatgi, P.K., 2015. Mechanical and tribological properties of self-lubricating metal matrix nanocomposites reinforced by carbonnanotubes (CNTs) and graphene: A review. *Compos. Part B Eng.* 77, 402–420.

and compared Young's modulus with various weight percentages of CNT and reveals that there was less significant in Young's modulus values up to 2 wt% fraction of CNT. A similar trend was witnessed for Young's modulus calculations with the maximum enhancement of 23% observed for the sample with the same weight fraction of CNT. However, Young's modulus was noted decreased slightly at 5 wt% but still exceeds the stiffness of pure aluminum matrix about 20%.

Wear and Friction Behavior

Mostly lubricant is applied externally to reduce the wear. This induces the complications when the materials want the periodic use of lubricant, particularly to wear parts which are difficult to access. For such applications, self-lubricating materials are ideal because the solid lubricant act automatically to reduce the wear. Graphite is one of the most common used solid lubricant materials. The aluminum graphite composite contains the small amount of graphite show better wear properties over the base materials but reduces the strength of the composite. [Choi *et al.* \(2010\)](#) revealed that MWCNTs were active reinforcement for improving wear due to its self-lubricating properties and other researchers also reported in their studies ([Bastwros *et al.*, 2013](#); [Al-Qutub *et al.*, 2013](#); [Moghadam *et al.*, 2015](#); [Kumar and Dhiman, 2013](#)). They found that the wear rate of the composite decreased progressively with the increase of CNTs content ranges from 0% to 20 % volume fraction. [Fig. 16](#) shows the effect of volume fraction of CNT on the coefficient of friction Al/CNT nano composite under the applied load of 30 N and sliding speed of 0.12 m/s.

The wear rate increases with an increase in porosity since pores act as a source of crack initiation and propagation lead to the excessive sub-surface cracking. Investigation of worn surfaces exposed that, at lower loads, abrasion was the leading wear mechanism and at higher loads adhesion was the leading wear mechanism for the monolithic alloy. Similarly, it was clear that the friction and wear behavior of Al/CNT composite mainly depends on the applied load and it is shown in [Fig. 17](#).

[Choi *et al.* \(2010\)](#) revealed that the coefficient of friction and the wear increased with increasing the load and reduced with increasing the speed of sliding. [Fig. 18](#) shows the relationship between the volume fraction on the wear rate of the composite under the sliding speed of 1.1 m/s and applied a load of 20 N.

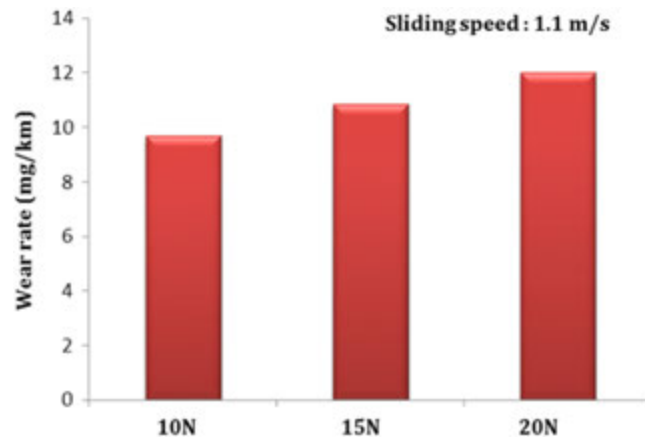


Fig. 17 Variations in wear rate of the Al/5 wt% CNT under different load conditions. Reproduced from Bastwros, M.M.H., Esawi, A.M.K., Wifi, A., 2013. Friction and wear behaviour of Al–CNT composites. *Wear* 307, 164–173.

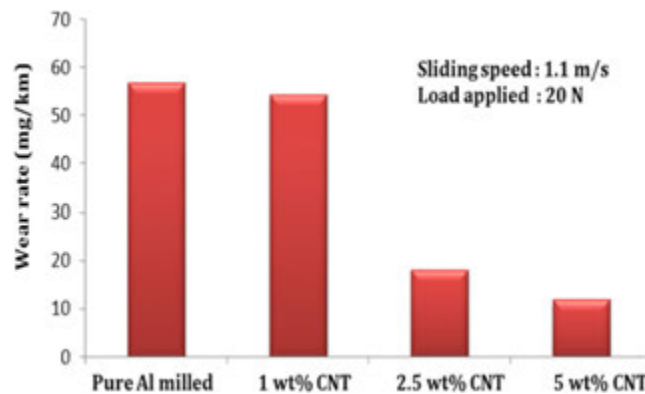


Fig. 18 Variations in wear rate of the composite concerning the CNT wt%. Reproduced from Bastwros, M.M.H., Esawi, A.M.K., Wifi, A., 2013. Friction and wear behaviour of Al–CNT composites. *Wear* 307, 164–173.

Fig. 19. indicates the worn surfaces of pure milled aluminum and aluminum with 5 wt% CNT. In CNT based composite, a film layer of carbon can cover the wear surface and act as a solid lubricant that reduces the coefficient of friction, and this effect minimize the generation of heat during sliding. It was also noted that a uniform distribution of CNT combined with better densification and improved hardness is required for effective wear behavior at higher CNT volume fractions.

Coefficient of Thermal Expansion (CTE)

The coefficient of thermal expansion reduced in the matrix by the progressive addition of nano-ceramic particles. Silicon carbide addition creates a better reduction in the coefficient of thermal expansion when compared to the addition of CNT. The thermal expansion reduces as the presence of reinforcements increased in the matrix and which can be clearly observed from the graph given in [Fig. 20](#).

Bonding between CNT and matrix is a crucial role in the CTE. It was observed that the increase in the percentage of CNT in the hybrid matrix leads to an increase in CTE, due to the poor bonding between CNT and the base matrix ([Thakur et al., 2007](#)). [Deng et al. \(2008\)](#) intimated that addition of 1 wt% MWCNTs in the 2024Al matrix decreased the CTE by 11%–12% as compared to pure aluminum which implies that carbon nanotube reinforced metal matrix composite may be a favorable materials with low coefficient of thermal expansion ([Deng et al., 2008](#)). The variations in the CTE between CNT and the matrix material can develop the huge number of dislocations in the hybrid composites. These dislocations create a barrier for the further movement of dislocation. This was observed as the reason behind the increase of the strength in the hybrid composite even with the addition of a very low volume of reinforcements.

Conclusions and Scope for Future Studies

Carbon nanotubes (CNT) along with ceramic reinforcements at the nanoscale level can significantly enhance the mechanical, thermal, and physical properties of the hybrid composites. The powder metallurgy technique is an very good process route for the

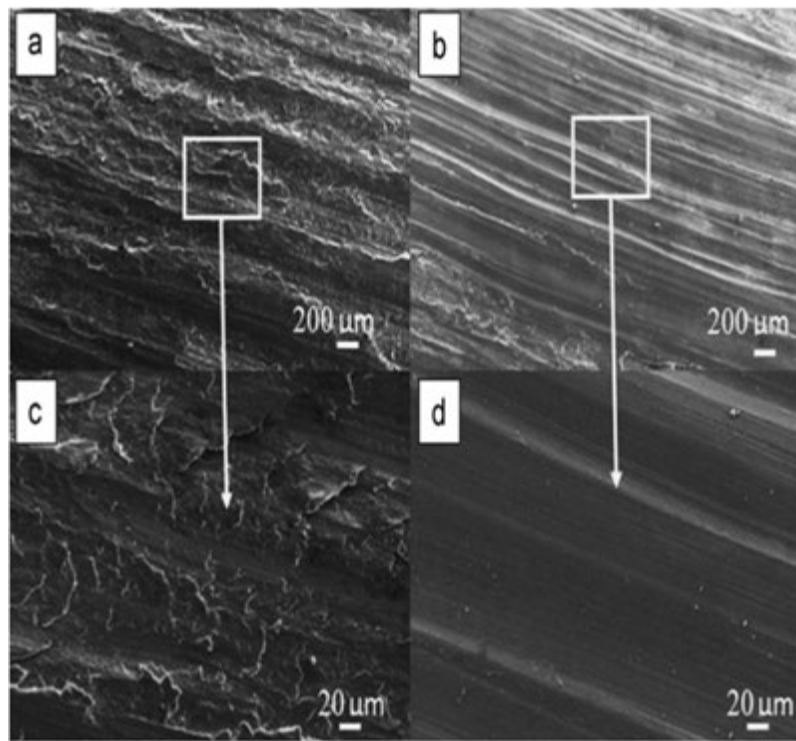


Fig. 19 SEM images showing the worn surfaces of (a) pure milled Al, (b) Al 5 wt% CNT, (c) and (d) are magnified areas of (a) and (b), respectively. Reproduced from Bastwros, M.M.H., Esawi, A.M.K., Wifi, A., 2013. Friction and wear behaviour of Al–CNT composites. *Wear* 307, 164–173.

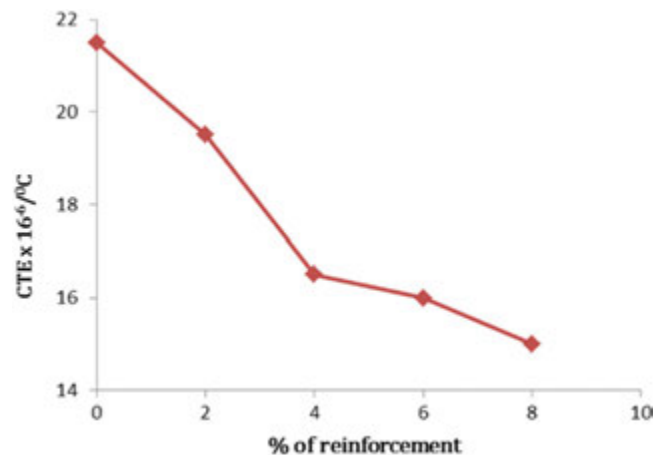


Fig. 20 Variation of Coefficient of thermal expansion with % reinforcement. Bodunrin, M.O., Alaneme, K.K., Chownb, L.H., 2015. Aluminium matrix hybrid composites: A review of reinforcement philosophies; mechanical, corrosion and tribological characteristics. *J. Mater. Res.* 4 (4), 434–445.

fabrication of CNT based hybrid metal matrix composite due to the flexibility in all stages of its processing. The processing conditions such as milling time, particle shape and size, aspect ratio, volume fractions, type of reinforcements, CNT dispersion, sintering time, and sintering temperature are prominently influences the microstructure and mechanical properties of the composites. Hence, optimization of these parameters is extremely important for obtaining better results. The strength of the composites mainly depends on the interface bonding between CNT and metal matrix. Strong bonding improves the load transfer effect. There is a lot of scope for further work in CNT based metal matrix composite production. Still, the homogeneous dispersion of CNT and wettability between the CNT and the matrix are the key challenges. Alignment and orientation of CNT in the matrix is the focusing area for the future studies. Carbide formation on the surface of the CNT based composites and clustering are other important areas for the further studies.

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Casting Routes for Production of Metallic Based Composite Parts

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Introduction

A composite material is a material system consisting of a mixture or combination of two or more nano-micro- or macro-based elements with a separating interface where the constituents differ in shape and in the chemical make-up and is essentially insoluble (Smith and Hashemi, 2008; Kala *et al.*, 2014). The dispersed phase of the mixture (combination) is typically referred to as the reinforcement whereas the continuous phase is known as the matrix (Kala *et al.*, 2014). Composites are categorized as metal matrix (MMC), polymer matrix (PMC), or ceramic matrix (CMC) composites depending on the chemical nature of the matrix phase. A metal matrix composite (MMCs) therefore consists of at least two components of which the matrix is a metal and the dispersed or reinforcement phase being either another metal, a ceramic or an organic compound. MMCs are of significant interest due the fact that various material properties may be modified and or designed for a specific purpose. These include physical characteristics such as density, thermal expansion and thermal diffusivity and mechanical characteristics such as tensile and compressive strength, tribological behavior, etc. The increasing demand for advanced materials especially in the aerospace and automotive industries is driving the growth in use of MMCs. Ideally metal matrix composites aim to provide both improved static and dynamic material properties by the introduction of a tough yet rigid material that is resistant to crack formation and propagation.

MMCs containing various types of ceramic particles have been produced by either solid state or liquid state methods (David Raja Selvam *et al.*, 2013). These include solid state methods such as mechanical alloying (Srinivasarao *et al.*, 2009) and powder metallurgy (Rahimian *et al.*, 2009), whereas the liquid state methods include stir casting (Kalaiselvan *et al.*, 2011), compocasting (Amirkhanlou *et al.*, 2011), squeeze casting (Xiu *et al.*, 2012), and spray deposition (Srivastava and Ojha, 2005).

The solid state methods may be subject to certain disadvantages that include reduced strength, high tooling cost, high material cost, limitations on size and shape, dimensional changes while sintering, changes in density and safety and health risks. The liquid state techniques typically involve mixing of ceramic particles into melts with certain significant benefits when compared to the solid state techniques. These include improved matrix to particle binding, easier matrix-structure control, ease of processing, and a closer to final geometry result (Hanumanth and Irons, 1993; Seo and Kang, 1995; Sahin *et al.*, 2002; Taha and El-Mahallawy, 1998). The casting routes are preferred mainly because they may have a significant effect on the MMCs mechanical and tribological behavior. Improved MMC properties require that the ceramic particles are efficiently incorporated and successfully bonded into the metal matrix (David Raja Selvam *et al.*, 2013).

MMC components are mainly used in the transport industries. These include aerospace and automotive components such as pistons, automotive disc brakes, connecting rods, cylinder heads, blades, cylinder liners, vane shafts, aircraft landing gear, bolts, valves, and structural shapes such as rods, beams, and tubes. Electrical contacts and brushes are also manufactured. The current article introduces the different casting methods with special emphasis on aluminum matrix composites (Rosso, 2006).

Stir Casting

During stir casting the particle reinforcement is typically distributed into the melted metal by rotational mechanical stirring. The key feature of this process is the mechanical stirring. A typical stir casting setup is presented in Fig. 1.

A graphite crucible is contained in the center of the furnace within an induction heating coil arrangement. Melting occurs within the graphite crucible. The mixing method is performed by a graphite mixer mounted on a steel mandrel powered by a variable speed AC motor. The mechanical stirrer is orientated along the main crucible axis. Its vertical position is continuously adjustable. A feeding hopper arrangement is used to add the ceramic powder and alloy components in the appropriate amount and time. To prevent contact with the molten metal, the steel mandrel is enclosed in a graphite sleeve. Glass fiber roving is used as heat insulation on the inside of the production unit. Argon gas is used both to insulate the molten metal from interacting with the atmosphere and to facilitate and regulate controlled addition of the reinforcement particles. Temperature control of the melt is facilitated by thermostat via internally and externally (crucible) mounted thermocouples (Kok, 2005; Mahadevana *et al.*, 2008; Deshmanya and Purohit, 2012). Stir casting is typically a cost-effective method of producing MMCs and suitable for mass production. It is also relatively simple and may produce components close to net shape. Stir casting is useful for the manufacture of products with numerous features and irregular contours (Chadwich and Heath, 1990).

The process parameters that may affect the mechanical and metallurgical characteristics of stir casts include the following; mold material, mold design, reinforcing particle feed rate, preheat temperature, temperature of the furnace, pouring method, properties of the matrix alloy, composition of matrix alloys, freezing range of matrix material, stirring speed, material of the stirrer, stirring time, impeller blade angle, and number of blades in the stirrer (Jebeen Moses *et al.*, 2016; Nai and Gupta, 2002; Naher *et al.*, 2003; Akhlaghi *et al.*, 2004; Prabu *et al.*, 2006; Ravi *et al.*, 2007; Amirkhanlou and Niroumand, 2010; Zhang *et al.*, 2010; Guan *et al.*, 2011;

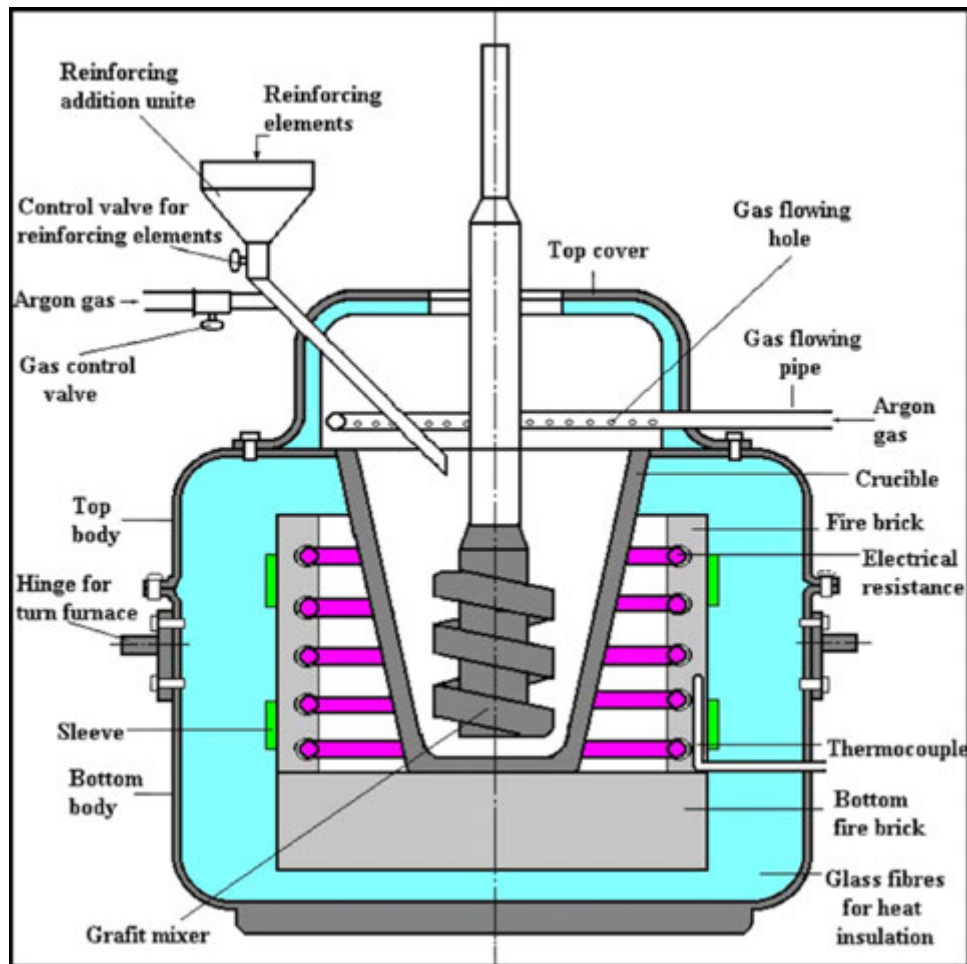


Fig. 1 Schematic diagram of a typical stir casting apparatus for the production of MMCs. Reproduced from Kok, M., 2005. Production and mechanical properties of Al_2O_3 particle-reinforced 2024 aluminium alloy composites. *Journal of Materials Processing Technology* 161, 381–387.

Sajjadi *et al.*, 2012a; Du *et al.*, 2012; Akbari *et al.*, 2013; Khosravi *et al.*, 2014). Typical problems that may manifest during stir casting include; non uniform distribution of reinforcing particles in the matrix, poor wettability between the matrix alloy and reinforcing particles, porosity and chemical reactions between the reinforcement and the matrix alloy. Stir casting is the most common technique for the manufacture of specifically aluminum matrix composites (AMCs). The aluminum matrix is typically fully melted and ceramic particles are added and mixed into the matrix by mechanical stirrer. Diverse techniques of improving wettability, including the addition of wetting agents and pre-heating and/or coating of the ceramic particles were attempted with varying success by researchers (Hashim *et al.*, 2001; Kerti and Toptan, 2008; Sahin, 2003; Ramesha *et al.*, 2009).

Sahin (2003) used stir casting to prepare AA2024/SiC AMCs. As reinforcement material, SiC particles with an average size of 110, 45 or 29 μm were used. In total, 10 and 20 wt% SiC particles were added. Before the melting process was initiated, SiC particles were oxidized at a temperature of 1100°C for 2 h. Between 5 and 8 g of SiC particulates, wrapped in aluminum foil packets, were selectively added into the molten metal upon formation of the molten pool vortex every 15–25 s. Upon insertion of the mixture packet it commences to melt thereby introducing the particulates into the melt. Stirring occurs after which the melt is poured into a pre-heated mold. This technique facilitates complete and homogeneous distribution of the particulates into the matrix. Optical micrographs of 10 wt% SiC strengthened AA2024 aluminum alloy are presented in Fig. 2(a)–(c). The SiC distribution in these composites is uniform.

The microstructure in Fig. 1(a) does not display the presence of any pores. This is due to the adequate wettability of the SiC and AA 2024 alloy combination. Fig. 2(b) displays a composite with a particle size of 45 μm . It once again displays no porosity or other cavities indicating effective bonding between the matrix and ceramic particulates. The same is true for the 110 μm particulate size (Fig. 2(c)). The particles do however display an angular shape and the presence of finer particles (also SiC) of less than 25 μm size. Fig. 2(d)–(f) display composites manufactured with a 20 wt% of SiC particles with sizes of 29 μm , 45 μm , and 110 μm , respectively. These micrographs indicate once again that these composites are free from porosity. A homogeneous distribution of the particles was achieved only for the 110 μm particle size. Limited agglomeration was visible for the other two sizes (29 μm , 45 μm).

Ashok Kumar and Murugan (2012) used stir casting to produce AA6061-T6–AlN composites. In order to increase the wettability, 2% (total composite weight) of magnesium was added when the temperature reached 1000°C. SEM micrographs of the

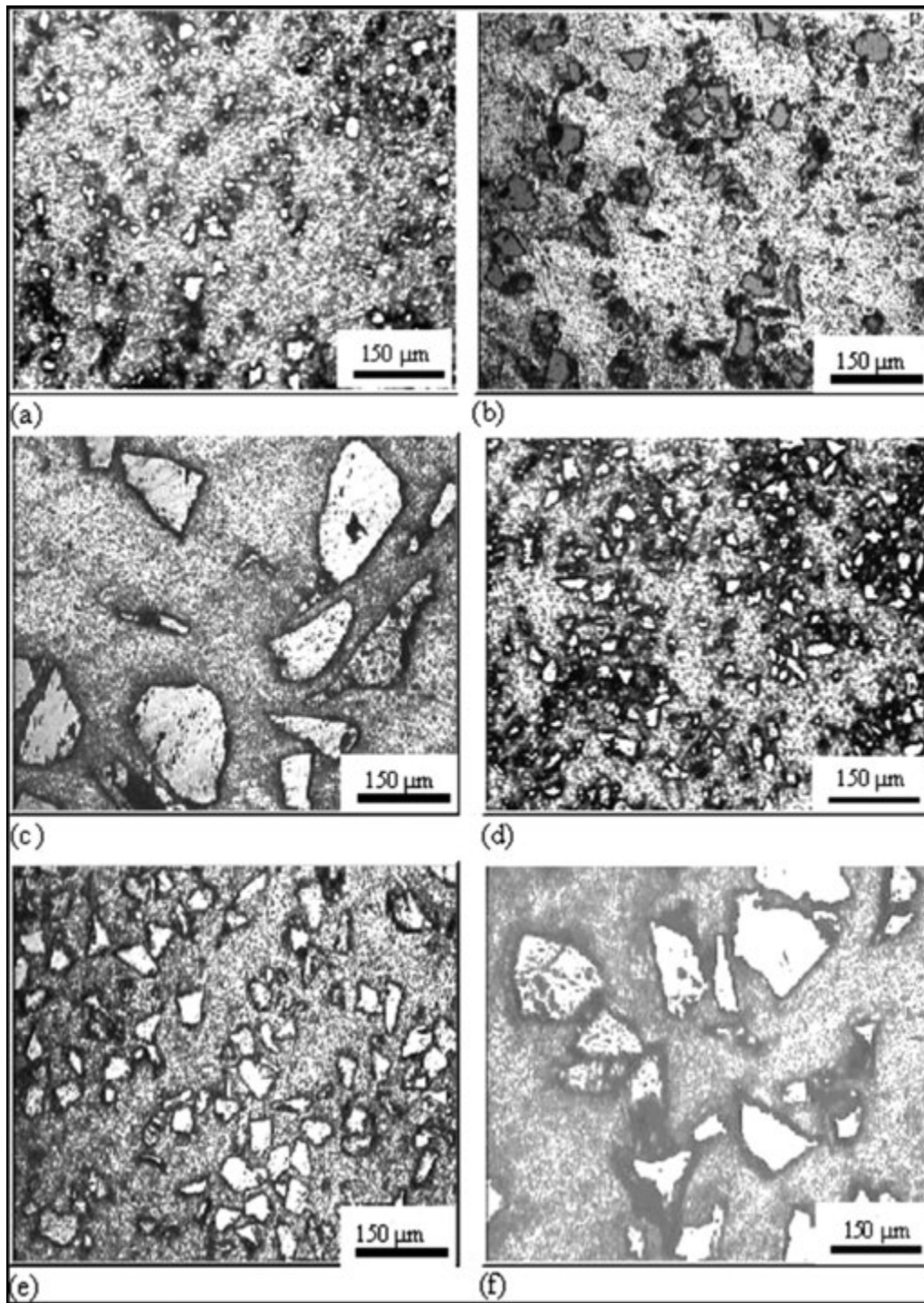


Fig. 2 Optical micrographs of metal matrix composites. (a) 10 wt% SiC with 29 mm particles; (b) 10 wt% SiC with 45 mm size; (c) 10 wt% SiC with 110 mm particles; (d) 20 wt% SiC with 29 mm; (e) 20 wt% SiC with 45 mm; and (f) 20 wt% SiC with 110 mm. Reproduced from Sahin, Y., 2003. Preparation and some properties of SiC particle reinforced aluminum alloy composites. *Materials & Design* 24, 671–679.

resultant AA6061–AlN composites comprising 5% AlN, 10% AlN, 15% AlN, and 20% AlN, respectively are presented in **Fig. 3(a)–(d)**. The SEM micrographs demonstrate a uniform distribution of the AlN reinforcement (AlN) in the alloy matrix (AA6061).

The SEM micrograph in **Fig. 3(e)** displays a distinct separation between the AA6061 alloy matrix and the AlN composite due to wettability issues. Adding magnesium improves the resulting wettability between the AlN particles and the AA6061 alloy matrix and increased effective interface regions.

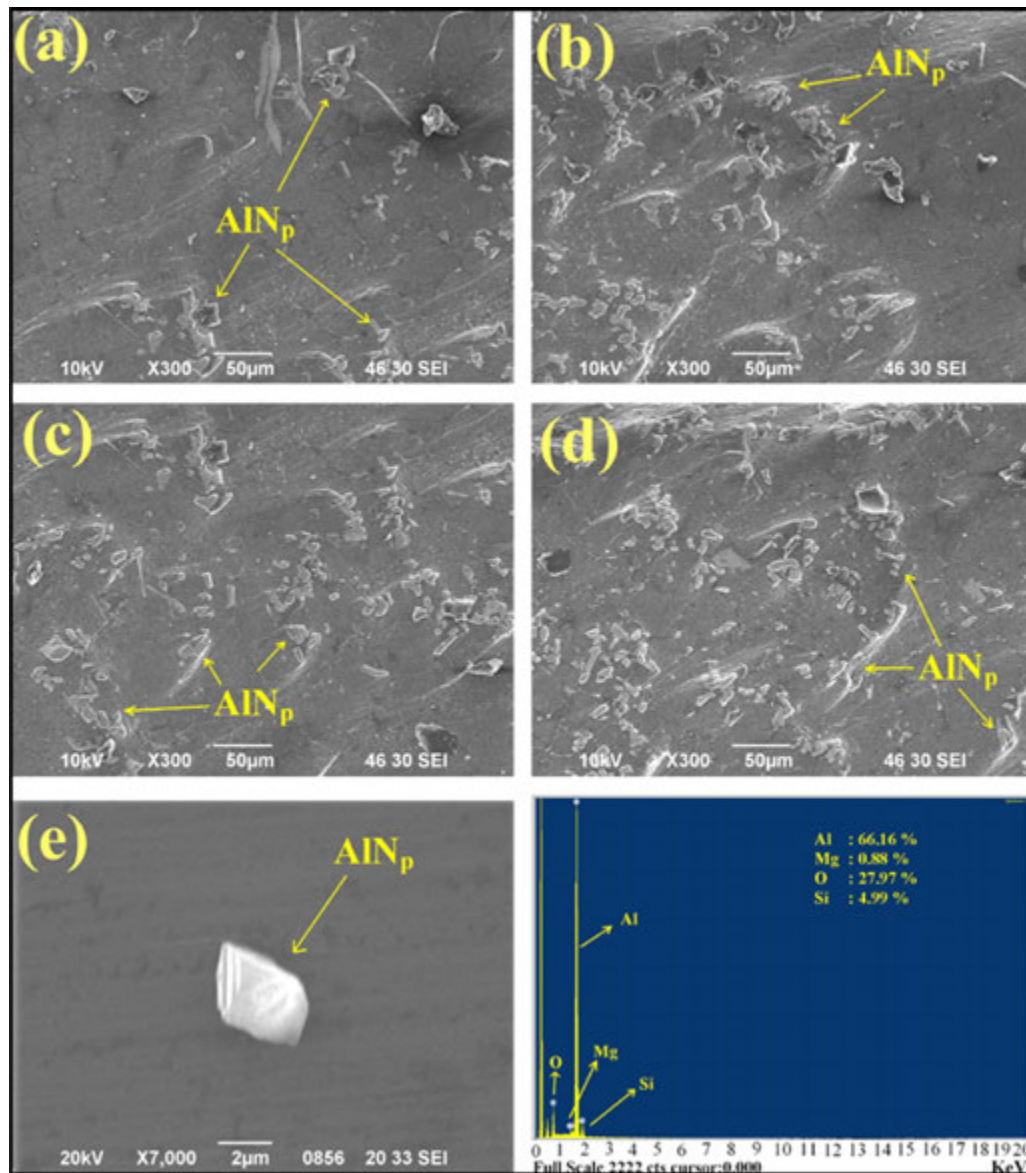


Fig. 3 SEM micrographs of AA6061–AlN composites containing: (a) 5% AlN, (b) 10% AlN, (c) 15% AlN, (d) 20% AlN, (e) 5% AlN, and (f) EDAX analysis of AA6061–AlN composites containing 20% AlN. Reproduced from Ashok Kumar, B., Murugan, N., 2012. Metallurgical and mechanical characterization of stir cast AA6061–Ti6–AlNp composite. Materials and Design 40, 52–58.

Ti was found to be an effective alloying element to improve wettability in the manufacture of Al/B₄C stir casting composites (Yu *et al.*, 2016a). It also limited the degradation of the B₄C particles (Kennedy, 2001, 2002). Fig. 4(a) presents a SEM back-scattered image of the composite at high magnification. The lighter regions (isolated and immediately surrounding the B₄C particles) were identified as Al₃Ti. A lower magnification image clearly displaying a uniform distribution of the B₄C particles (dark regions) within the Al–Ti master alloy is presented in Fig. 4(c). Fig. 4(e)–(h) presents the individual distributions of elements of Al, B, C, and Ti, respectively. It has been illustrated that the formation of TiB₂ layer limits the decomposition of B₄C particles and promotes their wettability in liquid aluminum, a breakthrough facilitating the production of Al/B₄C composites with stir casting method. The bonding between Al and B₄C during deformation is also quite stable. Fig. 4(i) illustrates the existence of fine light particles by the local Zone SEM image of Fig. 4(a). Elemental mapping findings are Fig. 4(j) and (k). Because the particles are far too small in comparison to the spot size of the energy dispersive spectrometer (EDS), Mg, and Si elements do not show discrimination appropriately. X-ray diffraction (XRD) pattern indicates the existence of Mg₂Si in Fig. 4(l). Combining the outcomes of X-ray fluorescence spectrometer (XFS), SEM, and X-ray diffraction (XRD), it is secure to assume that these fine light particles are Mg₂Si.

By adding Ti particles (Al₃Ti) and varying the stirring time, Yu *et al.* (2016b) produced Al/B₄C composites with enhanced wettability. Fig. 5 displays the particle distribution of the composites with variable levels of Ti and stirring time, with dark particles being B₄C and light particles being Al₃Ti.

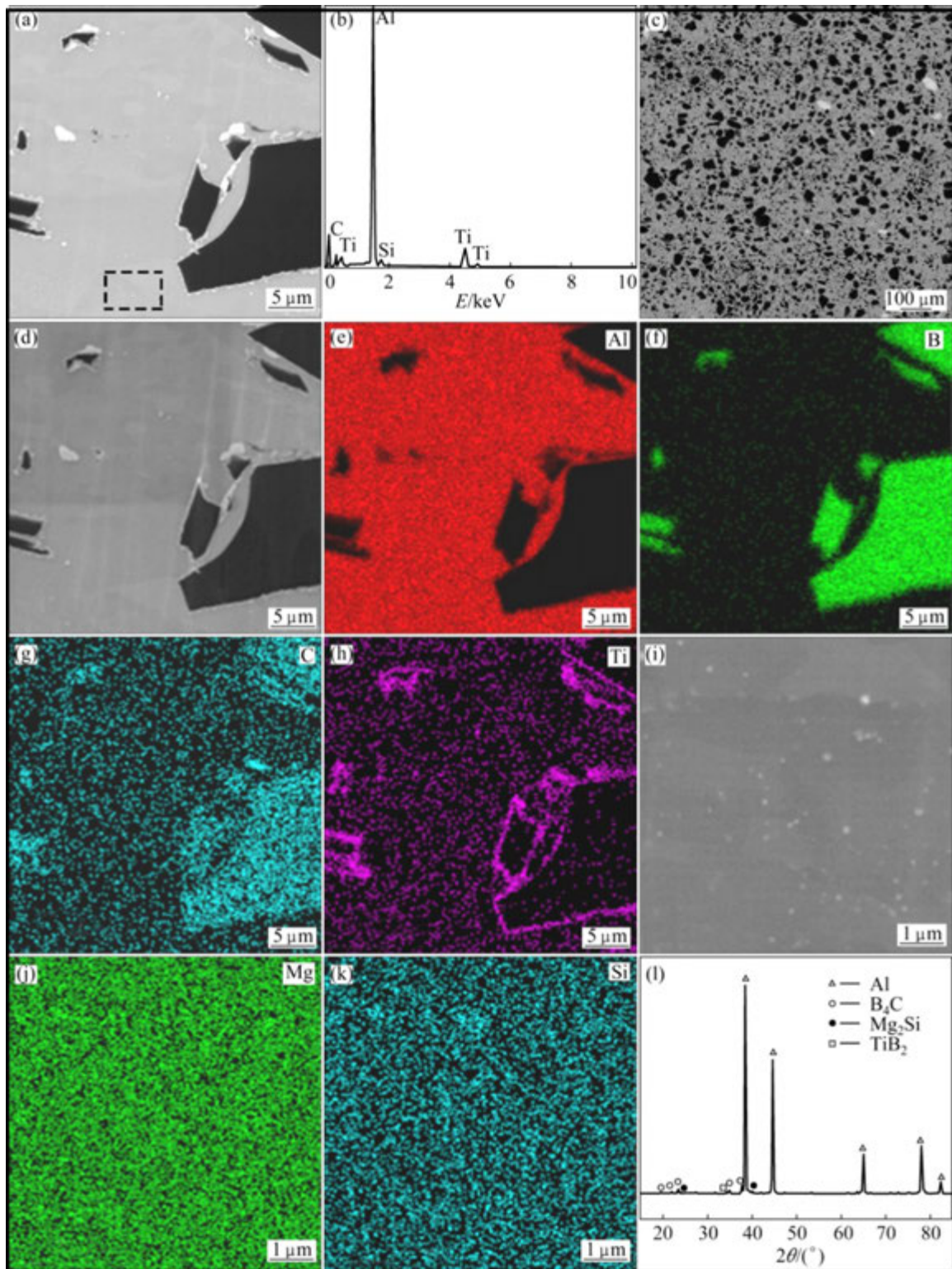


Fig. 4 Microstructures of AA 6061 – 31%B₄C composite: (a) High magnification SEM backscattered electron image; (b) EDS pattern; (c) Low magnification SEM backscattered electron image; (d) Low magnification electron image; (e – h) Al, B, C and Ti elemental mappings, respectively; (i) SEM image of local zone in (a); (j, k) Mg and Si elemental mappings, respectively; (l) XRD pattern showing the presence of TiB₂ and Mg₂Si in composite. Reproduced from Yu, L., Qiu-lin, L., Dong L., Wei, L., Guo-gang, S., 2016a. Fabrication and characterization of stir casting AA6061 – 31%B₄C composite Transactions of Nonferrous Metals Society of China 26, 2304–2312.

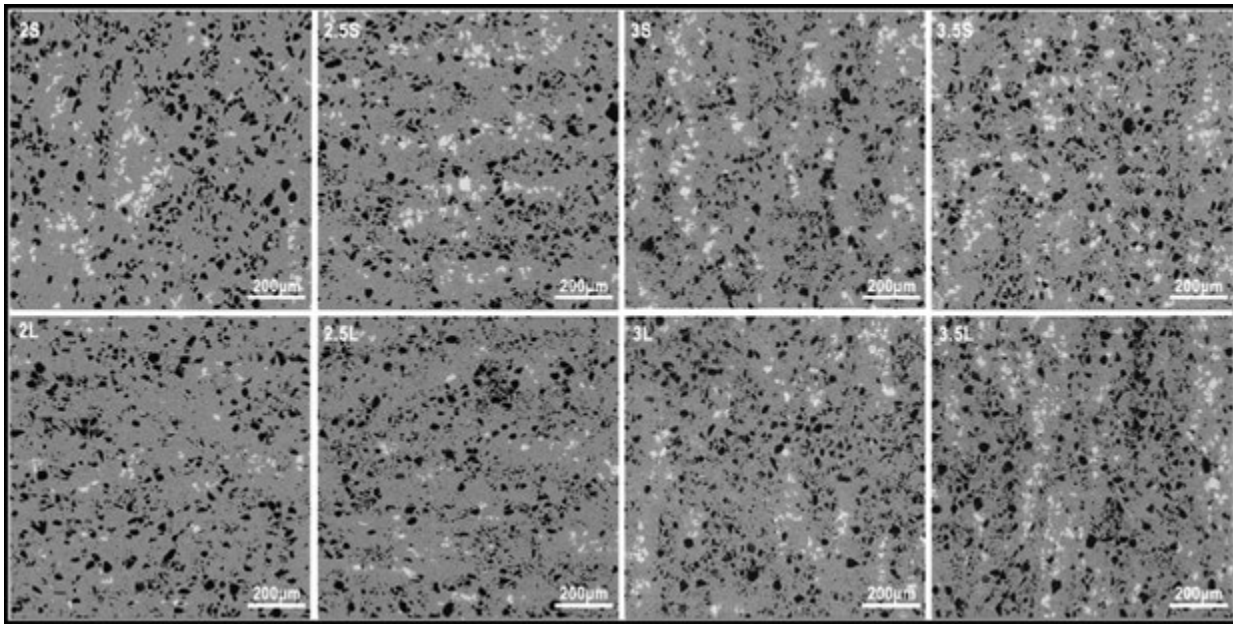


Fig. 5 B_4C Particle distribution of composites with different Ti levels and stirring time. Reproduced from Yu, L., Qiulin, L., Wei, L., Guogang, S., 2016b. Effect of Ti content and stirring time on microstructure and mechanical behavior of Al- B_4C composites. *Journal of Alloys and Compounds* 684, 496–503.

Ti atoms disassociate themselves from the Al_3Ti particles arising in both volume fraction reduction and particle size reduction of Al_3Ti . The reduced particulate size of Al_3Ti is advantageous due to its increased tensile strength (Manoharan and Lewandowski, 1992; Chawla and Shen, 2001).

The effect of stirring time and speed on the distribution of particles and the presence of porosity in the material matrix was investigated by Balasivanandha Prabu *et al.* (2006) when manufacturing Al–10% SiC composites. Their results are presented in Fig. 6. The results clearly indicated that the stirring time has a significant effect on the particle distribution. Increased stirring times are associated with a more homogeneous distribution of the particles. Particle clustering were evident in certain areas for the 5 min stirring time while other areas were mostly devoid of SiC particles. Increasing the stirring time to 10 and 15 min resulted in improved distribution. Increased stirring time along with increased stirring speed also resulted in an improved distribution of particles.

Jebeen Moses *et al.* (2016) investigated the effect of different blade angles to improve the mechanical and metallurgical properties of composites. Fig. 7 presents micrographs of AA6061/TiC composites formed at different blade angles. Micrograph Fig. 7(a) (blade angle of 0°) displays numerous clusters of TiC particles as well as particle-free regions.

TiC particles are agglomerated into selected regions adjacent to unreinforced regions. The vortex developed at a blade angle of 0° is shallow but sufficient for particle incorporation. The rate of particle mixing is slow. The angular velocity of the aluminum melt during mixing is too slow to induce sufficient flow of the melt. A flat and horizontal blade therefore does not produce the desired mixing and subsequent distribution. The micrograph (Fig. 7(b)) for a blade angle of 30° depicts a more homogeneous distribution of TiC particles in the aluminum matrix. Clustering, as apparent, for the 0° blade is not present. The results indicate that tilting the stirrer blade from the horizontal position yields improved distribution. The increase in blade angle increases the angular velocity of the aluminum melt and improves the centrifugal flow within the melt. The higher flow rates aid the break-up of the clusters and results in a more homogeneous distribution. Thus, the dispersion rate increases with increasing blade angle. Fig. 7(c) and (d) indicates the dispersion of the particles for the top and the bottom sections in a cast for a blade of 60° . The distribution of TiC particles across the depth of the casting from top to bottom is not constant. Few TiC particles are observed (Fig. 7(c)) at the top of the casting. On the other hand, TiC particles are distributed more uniformly at the bottom of the casting albeit with some stratification. The particle density is higher when compared to the results of the homogeneous distribution of the 30° blade angle (see Fig. 7(b)). This indicates that the particles are displaced downwards toward the bottom of the crucible resulting in an uneven particle density distribution. The resulting angular velocity of the 60° blade angle results in a significant axial variation in the flow rate. The molten aluminum above and below the stirrer is therefore subjected to different centrifugal flow rates (Naher *et al.*, 2003; Ravi *et al.*, 2007). The flow of the aluminum melt therefore becomes an intense swirl, dragging the TiC particles toward the bottom. Porosity is also noticed in micrographs in Fig. 7(c) and (d). The swirl motion draws more air into the aluminum melt and is subsequently trapped during solidification. The 30° blade angle was therefore demonstrated as the optimum to obtain the desired distribution.

Pozdniakov *et al.* (2017) developed an Al-5Cu/ B_4C composite for automotive applications. B_4C particles were preheated to $250^\circ C$ for 30 min and added manually while stirring, resulting in a uniform feed inside the vortex created by stirrer. Subsequently,

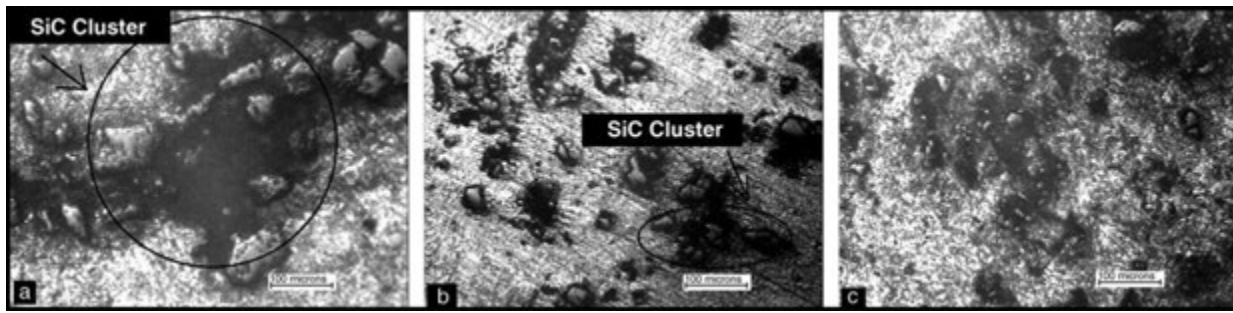


Fig. 6 Microstructure of Al–10% SiC_p MMC fabricated at 500 rpm: (a) 5 min stirring; (b) 10 min stirring; (c) 15 min stirring. Reproduced from Balasivanandha Prabu, S., Karunamoorthy, L., Kathiresan, S., Mohan, B., 2006. Influence of stirring speed and stirring time on distribution of particles in cast metal matrix composite. *Journal of Materials Processing Technology* 171, 268–273.

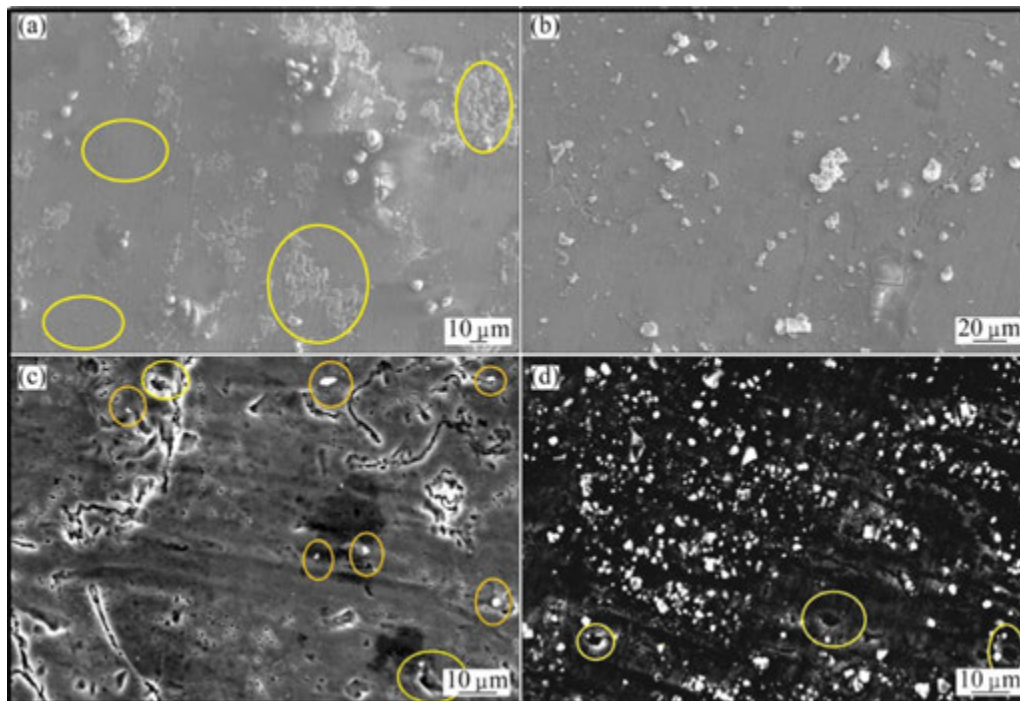


Fig. 7 FESEM (a, b) and SEM (c, d) images of AA6061/TiC AMCs at different blade angles: (a) 0° (clusters and particle free regions are circled); (b) 30° (C25); (c) 60° (TiC particles and pores are circled, top portion of casting); (d) 60° (pores are circled, bottom portion of casting). Reproduced from Jebeen Moses, J., Dinaharan, I., Joseph Sekhar, S., 2016. Prediction of influence of process parameters on tensile strength of AA6061/TiC aluminum matrix composites produced using stir casting. *Transactions of Non ferrous Metals Society of China* 26, 1498–1511.

the stirring was terminated and the temperature of the melt increased appropriately. Just before pouring, the melt was again stirred for 1 min and immediately cast into a graphite mold.

Fig. 8 presents the microstructure of the AMCs for different ratios of the reinforcing particles. In general, the micrographs indicate the presence of the Al solid solution, Al₂Cu eutectic phase (white), and B₄C particles (black). The distribution of the particles was uniform throughout the matrix with a few areas of reinforcement agglomeration. The authors reported that the extent of the agglomeration increased with increasing reinforcement ratio from 2% to 7% (Pozdniakov *et al.*, 2017).

Lekatou *et al.* (2015) prepared Al1050 based AMCs by the addition of submicron sized WC and TiC particles. Wetting and homogenization were improved by two approaches: fluxing and mechanical stirring.

K₂TiF₆ was utilized as a fluxing salt for removing the oxide phase from the surface of the aluminum melt (Baumli *et al.*, 2013; Toptan *et al.*, 2010). Mixing of the reinforcement and the salt was conducted first before this was added into the alloy melt (830°C). The salt was allowed to react with Al to form a slag, the carbide particles then infiltrated into the melt and the slag was removed by a ladle. Vigorous stirring was then applied for homogenization and dispersion of any initial particle clusters.

In the case of WC/Al, two types of tungsten aluminides were observed (**Fig. 9**): Al₁₂W in the form of coarse polygonal particles of largest diagonal of (3 – 18) μm (**Fig. 9(a)**) and Al₅W in the form of acicular plates (**Fig. 9(b)** and **(c)**). Al₃Ti particles appear as

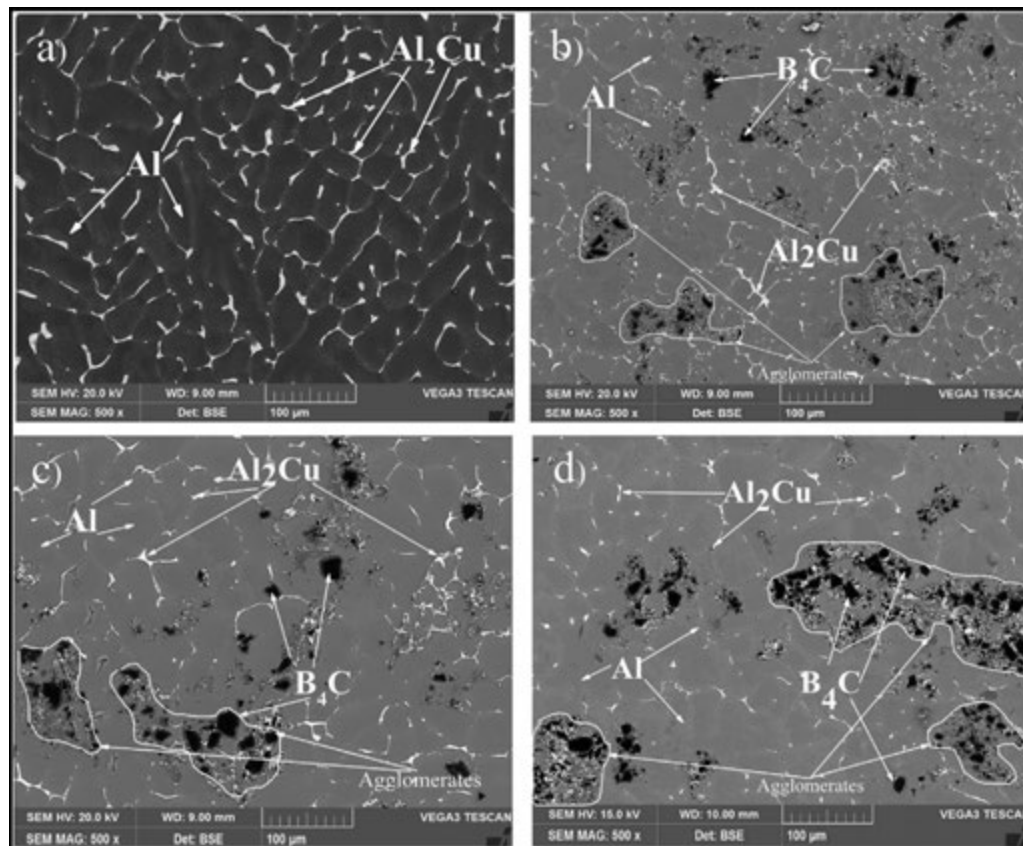


Fig. 8 Microstructure of matrix alloy (a) and Al-5%Cu-2%B₄C (b), Al-5%Cu-5%B₄C (c), Al-5%Cu-7%B₄C (d) MMCs under pressurized solidification. Reproduced from Pozdniakov, A.V., Lotfy, A., Qadir, A., *et al.*, 2017. Development of Al-5Cu/B₄C composites with low coefficient of thermal expansion for automotive application. *Materials Science & Engineering A* 688, 1–8.

clusters or agglomerates of fine rounded particles or as a system of coarse rectangular plates forming an incomplete rosette (**Fig. 9(c)**). A variety of different aluminide morphologies can result from the interaction of the Al-melt with the salt flux. Successful incorporation of particles is attributed: (a) the beneficial action of K₂TiF₆, which reacted with liquid Al to form a K–Al–F based liquid slag that removed surface oxide phases and allowed an improvement of the particle melt net wetting characteristics; and (b) the stirring applied during processing.

Karbalaei *et al.* incorporated different volume fractions of nano and micro TiB₂ particles into molten aluminum (A356) by a gas injector and mechanical stirrer (Karbalaei Akbari *et al.*, 2015). TiB₂ powders with average size of 5 μm and 20 nm were used as reinforcement powders. To achieve a uniform distribution of reinforcement powders in the molten alloy, a graphite stirrer was designed and used.

Fig. 10(a) displays a SEM image of modified silicon particles dispersed in heat treated A356 matrix. **Fig. 10(b)** shows agglomeration of nanoparticles on the interface of the silicon particle and aluminum matrix that can affect the aluminum matrix and silicon cohesion and acting as a preferential fracture point. **Fig. 10(c)** and **(d)** presents the distribution of the micro and the nano particle reinforcements. A uniform distribution of microparticles is observed in the microcomposite. Nanoparticle agglomeration is observed for the nanocomposite in of **Fig. 4(d)**. The authors observed that porosity increased with increasing reinforcement volume fraction and decreasing particle size. This process has some limitations such as wettability, interfacial reaction, porosity, low volume fraction, etc.

Table 1 presents details as regards to the tensile strength of various AMCs as regards to different reinforcement types, reinforcement volume fractions, and particle sizes.

Slurry Casting

Stir casting techniques have been among the simplest and the most economical processes of fabricating particulate metal matrix composites (Akhlaghi *et al.*, 2004; Mehrabian *et al.*, 1974). However, due to poor wetting of the ceramic particles by the molten alloy, the introduction and uniform dispersion of the reinforcement into the liquid matrix is challenging (Salvo *et al.*, 1994). Moreover, several structural defects such as extensive interfacial reactions (Salvo *et al.*, 1994), porosity and non-homogeneous

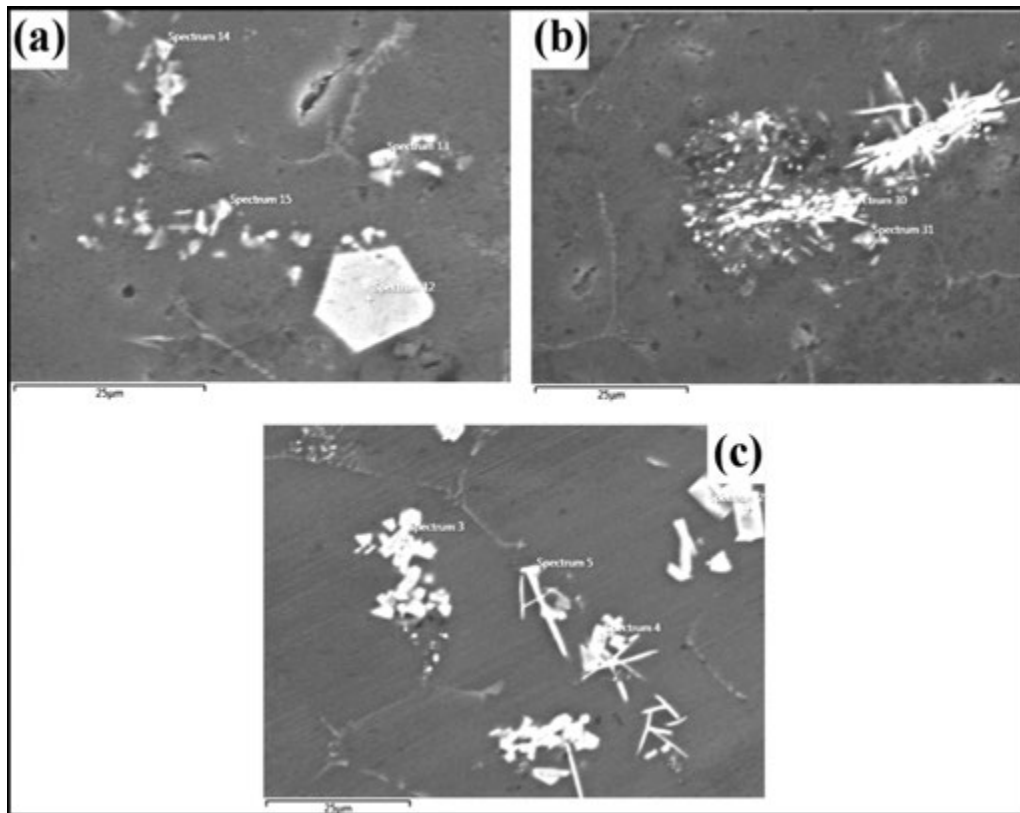


Fig. 9 Intermetallic compound particles observed in the WCp/Al materials (SE mode). Spot EDX analyzes in (at%): (a) spectrum 12: 91.73 Al-7.64 W-0.63 Ti, spectrum 13: 76.01 Al-18.47 Ti-5.52 W, (b) spectrum 29: 83.88 Al-15.55 W-0.57 Ti, and (c) spectrum 2: 75.44 Al-19.05 Ti-5.51 W, spectrum 3: 75.23 Al-18.95 Ti-5.82W, spectrum 5: 83.86 Al-15.03 W-1.11 Ti. Reproduced from Lekatou, A., Karantzalis, A.E., Evangelou, A., *et al.*, 2015. Aluminium reinforced by WC and TiC nanoparticles (ex-situ) and aluminide particles (in-situ): Microstructure, wear and corrosion behaviour. *Materials and Design* 65, 1121–1135.

particle distribution may arise due to the casting technique. In order to overcome some of the aforementioned drawbacks associated with the conventional stir casting techniques, semisolid agitation processes which are often referred to as slurry casting or Rheocasting or compo casting are being employed (Flemings, 1991). In the slurry casting processes, the reinforcement is added to a semisolid matrix alloy and the mixture is agitated vigorously. The presence of the primary solid phase in the viscous semisolid imposes an abrasive action on agglomerates of undispersed reinforcement in the slurry which assists the incorporation of the ceramic particles. The solidified metallic particles also prevent the non-metallics from settling, floating, or agglomerating, resulting in a more homogeneous particle distribution as compared with a fully molten alloy. Two variations of the slurry casting process namely semisolid–semisolid (SS) and semisolid–liquid (SL) processes are identified. They are distinguished from each other by the state of the matrix during the casting step, which is partially liquid or fully liquid for the SS and SL routes, respectively (Mehrabian *et al.*, 1974; Quaak and Kool, 1994; Hashim *et al.*, 2002). The most significant process parameters which influences the mechanical and metallurgical behavior of MMCs developed by slurry castings are as follows: (1) particle size (micro and nano) (2) weight percentage of the particles (3) pouring temperatures, (4) stirring time, (5) stirring speed, and (6) stirring temperature. The difficulties associated with this process is due to stirring within the freezing range and is described by Jebeen Moses *et al.* (2016) as follows. The binary phase equilibrium diagram of aluminum alloy AA6061 is presented in Fig. 11(a).

The magnesium and silicon in this aluminum alloy combines to form Mg_2Si . The amount of Mg_2Si is calculated using the chemical composition. The mass fraction of Mg_2Si is given by the vertical line in Fig. 11(a). The liquidus and solidus temperatures were estimated to be 655°C and 595°C, respectively. The alloy remains in a semi-solid state within this region. The liquid fraction of the aluminum alloy within the freezing range was computed using the lever rule from Fig. 11(a) and presented in Fig. 11(b). The liquid fraction at the casting temperature of 630°C is only 20%. It was however possible to stir the semi-solid slurry with difficulty and incorporate the particles. The distribution of TiC particles is related to the friction of the semi-solid slurry which depends upon the viscosity. The viscosity is relatively low at 630°C. Low viscosity is desirable to avoid undue vertical movement of particles. The frictional resistance is however high, which makes it impossible to distribute the TiC particles homogenously throughout the slurry. The poor flow rates within the slurry do not assist to disperse the particles, causing the formation of clusters. The presence of limited porosity is due to gas absorption by the semi-solid slurry being lower compared to the molten aluminum. A substantial portion of the semi-solid slurry is solidified at the instant of transferring to the mold. The possibility of solidification shrinkage

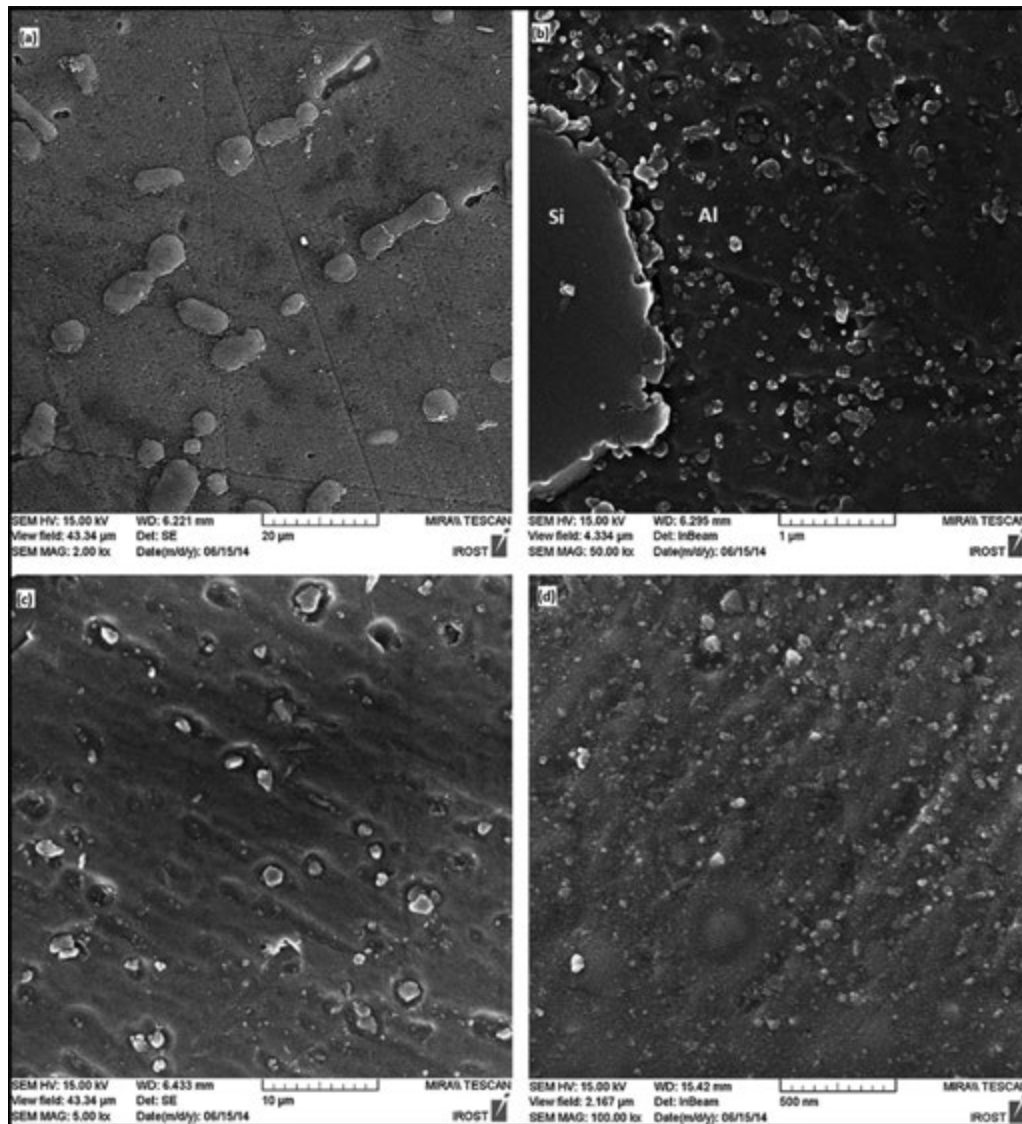


Fig. 10 SEM images of (a) modified silicon particles (b) agglomerated TiB_2 nanoparticles in silicon–aluminum matrix interface, (c) TiB_2 microparticle distribution and (d) TiB_2 nanoparticles in 1.5 vol% composites. Reproduced from Karbalaee Akbari, M., Baharvandi, H.R., Shirvanimoghaddam, K., 2015. Tensile and fracture behavior of nano/micro TiB_2 particle reinforced casting A356 aluminum alloy composites. *Materials and Design* 66, 150–161.

related porosity is remote. Since, the viscosity of the slurry is high; it cannot vent all the absorbed gas similar to a fully molten aluminum. Furthermore, the solidification rate is high at 630°C due to low latent heat and a high solid fraction. These two factors reduce the available time for the gas to escape, resulting in porosity.

Sohrabi Baba Heidary and Akhlaghi (2011) developed A356/SiC AMCs' by slurry casting. The SiC particles were artificially oxidized in air at 900°C for 120 min to form a layer of SiO_2 on the SiC particles. This SiO_2 layer results in the formation of MgAl_2O_4 phase at the Al-particle interface due to the presence of Mg in the alloy. Owing to the superior wettability of MgAl_2O_4 with molten aluminum as compared with SiC, this oxidation treatment improves the wettability of the reinforcing particles with molten aluminum and helps their incorporation while reducing undesired interfacial reactions. The oxidized SiC particles were classified, by sieving, into three size ranges: 45–53 μm , 90–106 μm , and 150–180 μm . In order to produce A356/SiC ingots, batches of the matrix alloy were melted to 720°C and then stirred at 550 rpm. The temperature was then gradually lowered until the melt reached a temperature in the alloy liquid-solid range (i.e., 590°C) while stirring was continued. The stirrer was positioned just below the surface of the slurry and the oxidized particles were added uniformly. These oxidized SiC particles were pre-heated at 300°C to evaporate the water that might be absorbed on their surface and to prevent chilling of the alloy during particle addition. During the addition of the SiC particles, the melt was alloyed with 1% Mg to improve the wettability of SiC particles. At the conclusion of charging, the slurry was allowed to mix at 300 rpm in the semi-solid state isothermally for another 10 min while the stirrer was positioned near the bottom of the crucible. The slurry was then heated to 680°C to properly maintain the fluidity of

Table 1 Tensile strength of AMCs with different reinforcement types, reinforcement volume fractions, and particle sizes

S.No	Matrix	Reinforcement type	Volume fraction	Size	Tensile strength (MPa)	Reference
1	Al6061	SiC	10%	45 μm	450	Davidson and Regener (2000)
2	Al356	B ₄ C	15%	< 30 μm	210	Shirvanimoghaddam <i>et al.</i> (2016)
3	AA 7075	B ₄ C	5%	50 μm	260	Verma and Vettivel (2018)
4	AA 6082	WC	8%	(53–75) μm	190	Ravikumar <i>et al.</i> (2017)
5	Al – 4.5% Cu	Fly ash + SiC	15%	10 μm	118	Mahendra and Radhakrishna (2010)
6	Al6082	Gr	0%	50	161.5	Sharma <i>et al.</i> (2016)
7	AA6063	SiC	10%	17–20 μm	180.61	Balasubramanian and Maheswaran (2015)
8	Pure aluminum	B ₄ C	15%	23.157 μm	136.45	Zhang <i>et al.</i> (2010)
9	Al LM6	TiC	15%	325 mesh size	323	Sivananth <i>et al.</i> (2014)
10	A359	Al ₂ O ₃ /2p	8%	30 μm	148.7	Kumar <i>et al.</i> (2013)
11	AA6061	B ₄ C	31%	23 μm	340	Yu <i>et al.</i> (2016a)
12	8011 Al	SiCp	15%	–	266	Vembu and Ganesan, 2015
13	AA7050	B ₄ Cp/SiCp	10%	20 μm	255	Ranjith <i>et al.</i> , 2017
14	7075	B ₄ C/ coconut shell fly ash	9%	75/ 62 μm	189	Subramaniam <i>et al.</i> (2018)
15	AA6061	TiC	15%	2 μm	220	Jebeen Moses and Joseph Sekhar, 2006
16	Al	Quartz particulate	6%	30–100 μm	129	Seah <i>et al.</i> (2003)

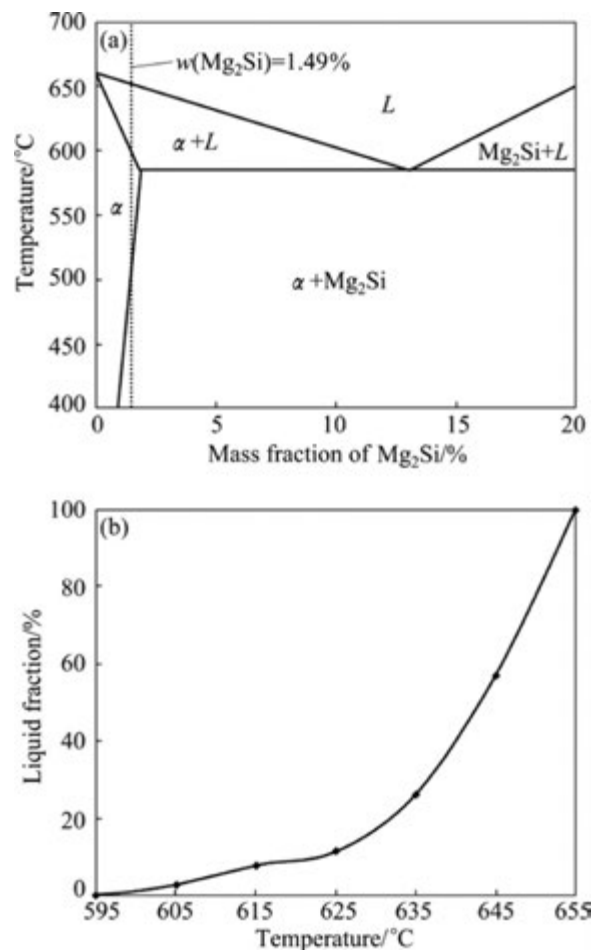


Fig. 11 Binary phase equilibrium diagram of Al – Mg₂Si system (a) and liquid fraction of AA6061 alloy within freezing range (b). Reproduced from Jebeen Moses, J., Dinaharan, I., Joseph Sekhar, S., 2016. Prediction of influence of process parameters on tensile strength of AA6061/TiC aluminum matrix composites produced using stir casting. Transactions of Nonferrous Metals Society of China 26, 1498–1511.

the molten metal, and kept at this temperature for 5 min while being continuously stirred. It was then poured into permanent cylindrical steel molds. By using the above-mentioned procedure, different composite ingots of 15 vol% SiC (45–53 μm), 25 vol% SiC (90–106 μm) and 30 vol% SiC (150–180 μm) were produced. These ingots were then remelted and diluted with the required

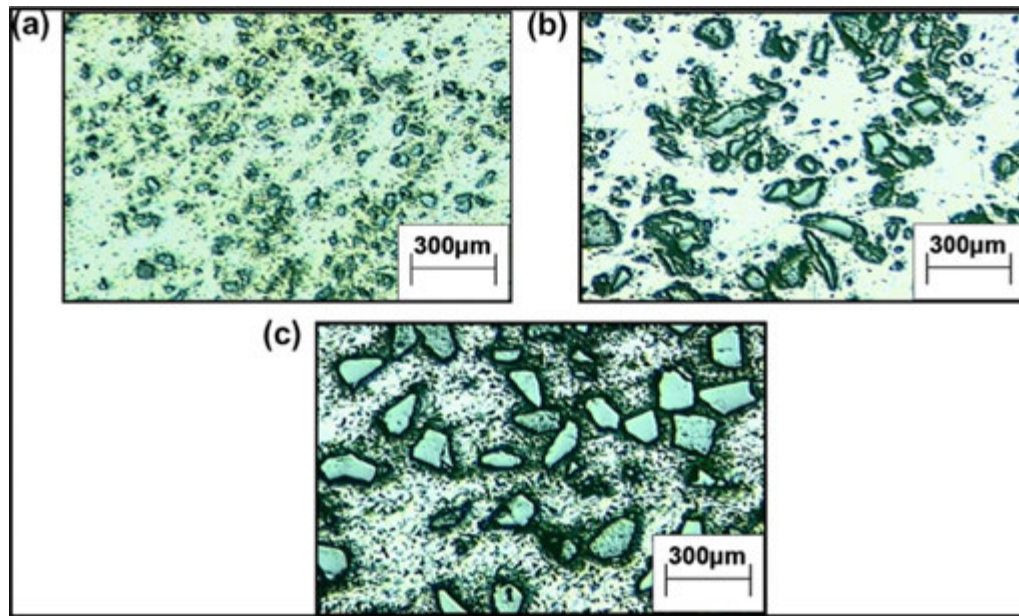


Fig. 12 Typical micrographs of Al/SiC composite ingots containing 15% of different sized SiC particles: (a) 45–53 μm , (b) 90–106 μm and (c) 150–180 μm . Reproduced from Sohrabi Baba Heidary, D., Akhlaghi, F., 2011. Theoretical and experimental study on settling of SiC particles in composite slurries of aluminum A356/SiC. *Acta Materialia* 59, 4556–4568.

amounts of A356 alloy to produce the desired composites with different concentrations. Typical micrographs of composite ingots containing 15% of different sized SiC particles are shown in **Fig. 12**.

Ceschini *et al.* produced 7005 aluminum alloy reinforced with 10 vol% of Al_2O_3 particles (W7A10A) and 6061 aluminum alloy reinforced with 20 vol% of Al_2O_3 particles (W6A20A) (Ceschini *et al.*, 2006). The different particle sizes as used in the composites are clearly visible **Fig. 13(a)** and **(b)**. In both composites, the Al_2O_3 particles were of non uniform size, irregularly shaped, and randomly dispersed in the alloy matrix. Agglomeration or clustering of the particles was also observed, resulting in particle-rich and particle-depleted regions. The homogeneity is generally higher in discontinuously reinforced composites (DRA–MMCs) manufactured by molten metal processes when compared to those produced by powder metallurgy (Lloyd, 1994; Torralba *et al.*, 2003).

Fig. 14 shows SEM images of 10% SiC/Al–Mg composites developed by Lin, *et al.* (2010) with addition of different Mg contents. They used four steps, firstly, SiC particles were preheated, secondly, the molten Al–Mg alloy was quickly poured into the crucible and then the melt temperature was dropped to the semi-solid temperature range. In the third step the semi-solid alloy and preheated SiC particles were stirred before the semi-solid mixture temperature was raised and further stirred during the fourth step. Finally, the mixture was poured into a preheated mold and a pressurized by mechanical means.

The pressure was maintained during solidification. A homogenous distribution of the SiC particles was obtained. In general composites with a higher Mg content display improved homogenous distribution (Lin *et al.*, 2010). The mechanical stirring during the semi-solid state accelerates the dispersion of the particles in the matrix due to a significant frictional force generated between the solid matrix particles and SiC particle reinforcement. By comparison, increasing Mg content, the particle distribution can be further improved because of the improved wettability between the matrix and reinforcement (Hashim *et al.*, 2001; Mitra *et al.*, 2004).

Fabrication of metal matrix composites with alumina particles by casting processes is usually difficult because of the very low wettability of alumina particles and agglomeration which results in non-uniform distribution and weak mechanical properties (Sajjadi *et al.*, 2012a,b). Sajjadi *et al.* (2012a) used stir and campo casting to produce A356 aluminum alloy matrix composites with micro and nano-size alumina particles. They reported that due to the good wettability the grain size of the composite fabricated by compo-cast was smaller than that of the stir-cast process. **Fig. 15** presents SEM micrographs displaying the distribution of alumina particles in different specimens.

Fig. 15(a) shows a good distribution of particles along with low agglomeration for the 1 wt% Al_2O_3 nano-composite fabricated by compo-casting. Moreover, the figure indicates that the Al_2O_3 nano-particles have a tendency to segregate and cluster at interdendritic regions which are surrounded by eutectic silicon (**Fig. 15(b)–(d)**).

Amirkhanlou and Niroumand (2012) injected the reinforcement particles into the melt in three different forms, i.e., as the as-received and untreated SiC, as particulate Al–SiC, and as Al–SiC–Mg composite powders. The effects of the type of the injected powder on the microstructure of the alloy are presented in **Fig. 16** (Mahadevana *et al.*, 2008).

SEM examination of the Al356–SiCp specimen (**Fig. 16(a)**) demonstrated significant gas porosity throughout the specimen and frequent clustering of SiC particles around these pores. As shown in **Fig. 16(b)** and **(c)**, a much better distribution of the reinforcement was obtained when the reinforcement was injected in the form of composite powders. It is believed that the

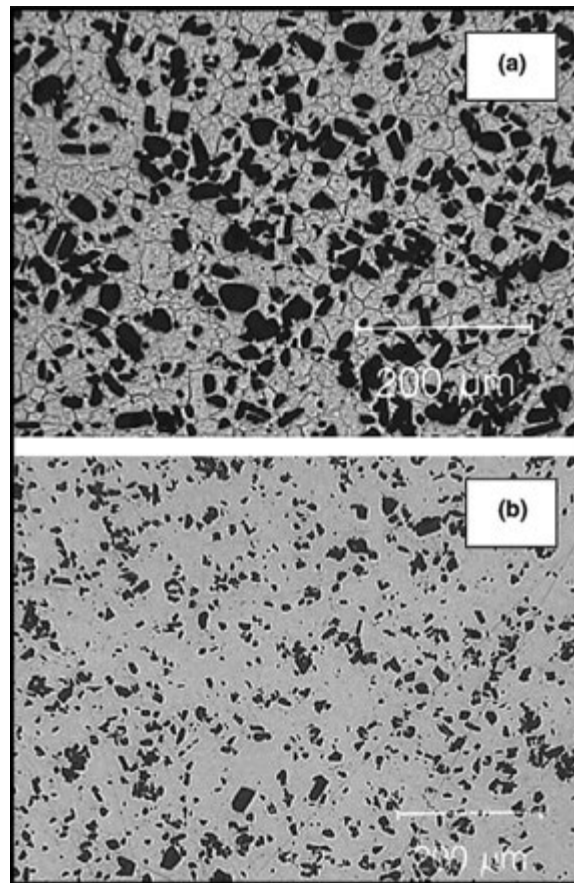


Fig. 13 Optical micrographs of the AA7005/10 vol% Al_2O_3 (a) and AA6061/20 vol% Al_2O_3 (b) composites. Reproduced from Ceschini, L., Minak, G., Morri, A., 2006. Tensile and fatigue properties of the AA6061/20 vol% Al_2O_3 p and AA7005/10 vol% Al_2O_3 p composites. *Composites Science and Technology* 66, 333–342.

expected gradual release and improved wetting of individual SiC particles with the molten matrix have greatly improved the uniform dispersion of the reinforcement in the Al356 molten matrix. **Fig. 16(c)** demonstrates a uniform distribution and negligible agglomeration of SiC particles in the matrix of the Al356–(Al–SiC–Mg)cp specimen. For this specimen the magnesium was added to the injected composite powder and not directly to the melt. Magnesium in these regions can react with the oxygen present on the surface of the SiC particles, narrowing the potential gas layer on the SiC and reducing the surface tension, thus improving the wetting and reducing the agglomeration tendency of the SiC particles (Hashim *et al.*, 2001).

Furthermore, addition of magnesium in the form of composite particles may also improve the magnesium recovery, which in turn improves the wetting and dispersion of SiC particles compared to the case where magnesium is added as an alloying element.

Hu *et al.* (2016) manufactured AMCs of A356/ B_4C using the slurry casting process, the effect of Ti on the interfacial reactions and bonding between the B_4C particles and matrix were studied and discussed. SEM images of the microstructure of the A356– B_4C AMCs with different particle sizes by the semi-solid stir casting process are presented in **Fig. 17**.

Without Ti additions, the shape and edges of particles became rounder and significant reaction compounds could be observed in specimens without addition of Ti elements (**Fig. 17(a)** and **(c)**). However, with Ti additions, B_4C particles were surrounded by Ti-rich reaction compounds (**Fig. 17(b)**), B_4C particles were even enclosed by the Ti-rich layer, as shown in **Fig. 17(d)**. Therefore, it can be concluded that the decomposition of B_4C was prevented by the Ti additions during the semi-solid stir casting process. It was also reported that B_4C particles of large size caused micro-voids to form at the particle-matrix interface indicating incomplete wetting (**Fig. 17(a)** and **(b)**), which would lower the interfacial bonding strength.

Allwyn Kingsly Gladston *et al.* (2015) produced rich husk ash (RHA) particulate reinforced AA6061 aluminum alloy composites by compocasting. SEM micrographs of AA6061/RHA AMCs at higher magnification are shown in **Fig. 18**. A clear interface is observed between the aluminum matrix and the RHA particles.

The interface is free from reaction products. The shape of the particle is similar to the original shape. There is no interfacial reaction or decomposition of RHA particles during compocasting. The interfacial reaction tends to affect the metallurgy of the matrix alloy. If reaction products surround particles, the load will not be effectively transferred to the particle. The load bearing capacity of the interface will be reduced. A clean interface enhances the load bearing capacity. Furthermore, the particles are not surrounded by pores or voids or micro cracks. RHA particles are completely wetted by the semi solid aluminum. They can be

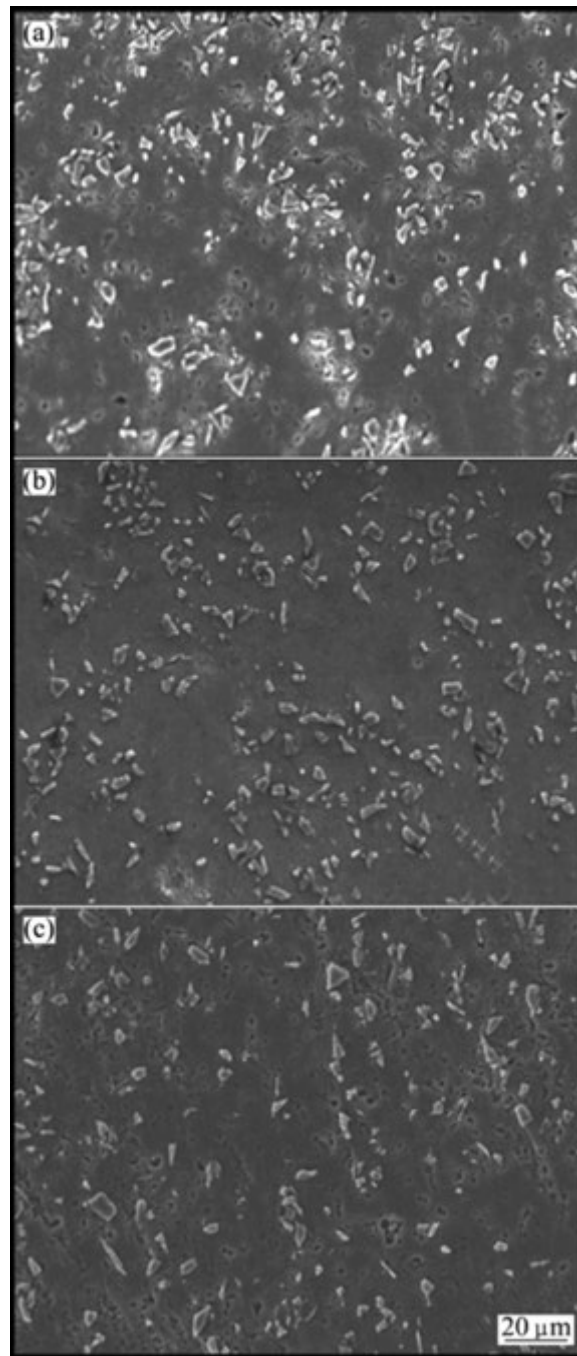


Fig. 14 SEM images of 10% SiC/Al-Mg composites: (a) SiC/Al-2.5Mg; (b) SiC/Al-4.2Mg; (c) SiC/Al-6.8Mg. Reproduced from Lin, G., Wei, Z.H., Ze, L.H., Na, G.L., Jun, H.L., 2010. Effects of Mg content on microstructure and mechanical properties of SiCp/Al-Mg composites fabricated by semi-solid stirring technique. Transactions of Nonferrous Metals Society of China 20, 1851–1855.

considered as well bonded with the matrix. This in turn reduces the possibility of the pull-out of RHA particles during tensile loading. Stirring issues, porosity, and low volume fraction of reinforcement etc., are drawbacks of this method. [Table 2](#) presents selected details about tensile behavior of different composites produced by slurry casting.

Centrifugal Casting

Centrifugal casting is one of the potential manufacturing techniques to produce near net shaped components with improved properties. Functionally graded materials (FGMs) are defined as special materials that can be purposefully processed to obtain

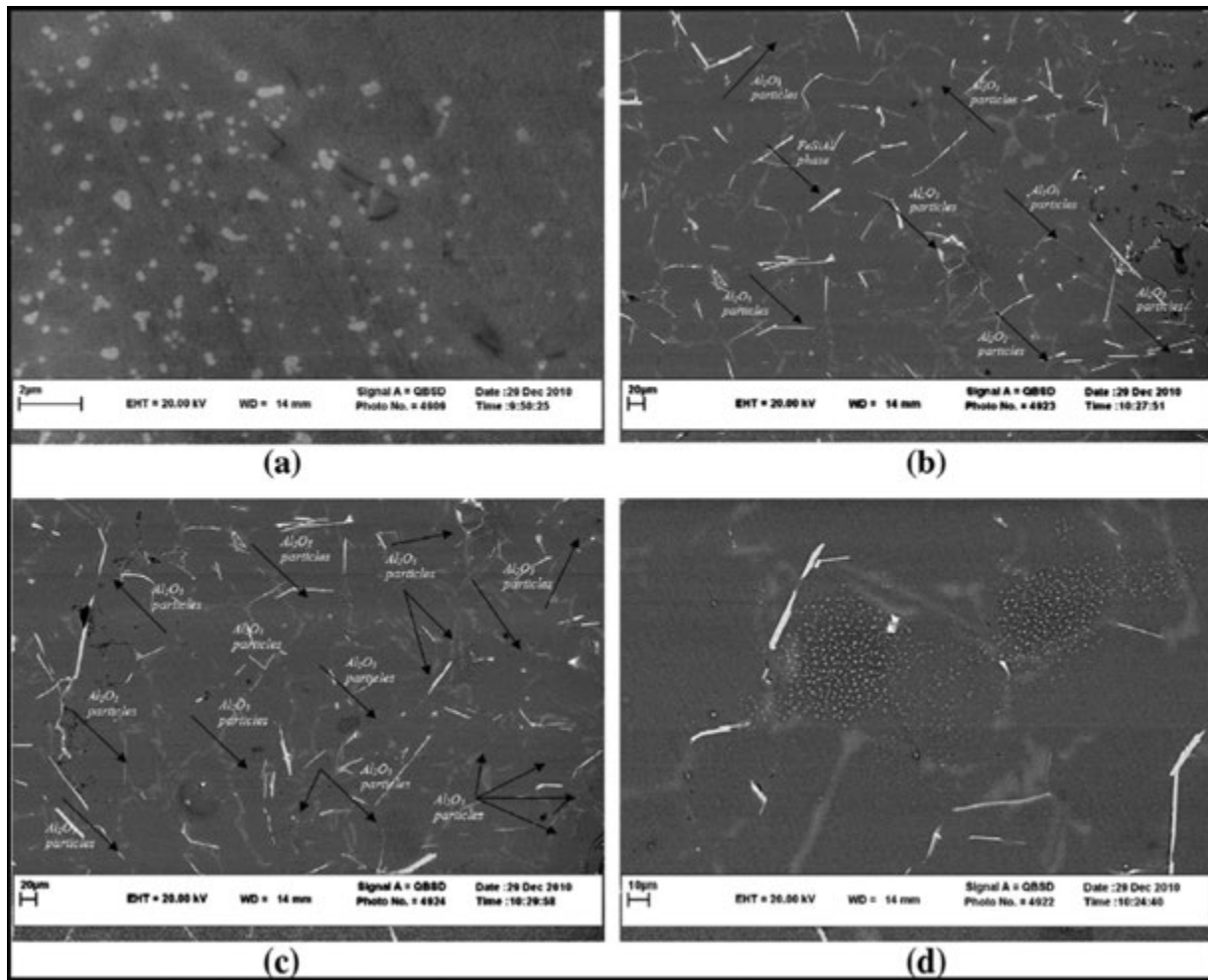


Fig. 15 SEM micrographs of nano-composites reinforced with: (a) 1 wt% Al_2O_3 ; (b) 2 wt% Al_2O_3 ; (c) 3 wt% Al_2O_3 ; fabricated by compo-casting process; and (d) 1 wt% Al_2O_3 ; fabricated by stir-casting process. Reproduced from Sajjadi, S.A., Ezatpour, H.R., Parizi, M.T., 2012a. Comparison of microstructure and mechanical properties of A356 aluminum alloy/ Al_2O_3 composites fabricated by stir and compo-casting processes. *Materials & Design* 34, 106–111.

discrete or continuously varying compositions over a definable geometrical length (Hadad *et al.*, 2010; Fukui and Watanabe, 1996). These FGMs, wherein the intermetallic compound has a higher density than the matrix, are best fabricated by the centrifugal method (Watanabe *et al.*, 1997; Sequeira *et al.*, 2005). Centrifugal casting is the process, where molten metal is poured into a rotating or spinning mold to solidify it to a desired shape by the high compressive pressure exerted by the centrifugal acceleration. It provides castings with refined microstructures, enhanced mechanical properties, limited presence of inclusions and porosity (Arsha *et al.*, 2015). A set of experiments was performed using a horizontal type centrifugal casting machine shown in Fig. 19.

The process uses the radial forces generated due to the centrifugal acceleration to segregate the discrete second phase from the matrix of composite materials. When a particle containing slurry is subjected to a centrifugal acceleration, two distinct zones of particle enrichment and depletion are formed. The extent of particle segregation and the associated enrichment and/or depletion locations within the casting is mainly dictated by the melt temperature, metal viscosity, cooling rate, the densities of the particles and liquid, particle size, and the magnitude of the centrifugal acceleration. Depending on the density of particles, the lighter particles segregate toward the axis of rotation, while the denser particles move away from the axis of rotation. Centrifugal casting is widely used to produce high speed rotating or reciprocating mass items such as pistons, connecting rods, drive shafts, brake rotors, and cylinder liners.

Generally (Hadad *et al.*, 2010), fabrication of FGMs by the centrifugal method is classified into two categories based on the processing temperature of the master alloy. If the processing temperature is lower than the liquidus temperature of the alloy, the reinforcement particle remains solid in a liquid matrix. This method is referred to as a centrifugal ex situ method (Fukui and Watanabe, 1996; Watanabe *et al.*, 1997). On the other hand, if the processing temperature is higher than the liquidus temperature of the alloy, both of the reinforcement particle and the matrix are subject to centrifugal acceleration during solidification. This solidification is similar to the production of in situ composites using the crystallization phenomena, and is, therefore, referred to as a centrifugal in situ method (Watanabe *et al.*, 2001; Fukui *et al.*, 1994, 1997; Watanabe and Oike, 2005).

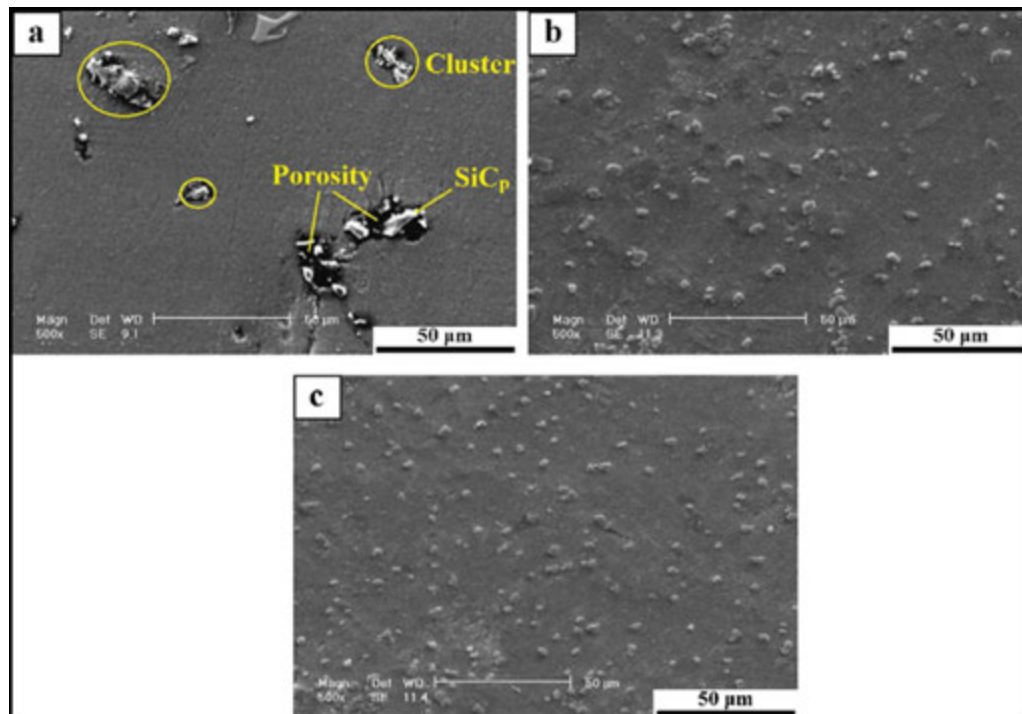


Fig. 16 Typical SEM microstructures of different samples: (a) Al356-SiC, (b) Al356-(Al-SiC), and (c) Al356-(Al-SiC-Mg). Reproduced from Amirkhanlou, S. and Niroumand, B., 2012. Fabrication and characterization of Al356/SiCp semisolid composites by injecting SiCp containing composite powders. *Journal of Materials Processing Technology* 212, 841–847.

Rajan *et al.* (2008) presented work on processing and characterization of functionally graded Al matrix composites components based on Al-SiC ex situ and Al-Si in situ composites. In the case of Al-SiC functionally graded metal matrix composites disks, the particles are segregated such that a density gradient occurred toward the outer periphery of the casting where increased strength and hardness were apparent toward the outer periphery. The Al-Si in situ composite cylinder displayed the dispersion of primary Si particles toward the inner periphery of the casting which can lead to higher hardness and wear resistance.

Fig. 20 presents an example of a Al-SiC disc fabricated by ex situ centrifugal casting. Visual and ultrasonic inspection of the disc has shown a largely porous free area toward the outer periphery. An example of an in situ formed primary Si reinforced functionally graded Al matrix composite hollow cylinder is shown in Fig. 20(b). The relevant process parameters associated with centrifugal castings are numerous and include centrifugal radius, rotational speed, type of caster, casting atmosphere, mold temperature, pouring temperature, pouring rate, thermal gradient through the mold, velocity of mold rotation, and solidification rate. An increased centrifugal radius and higher rotational speed increases the volume fraction of particles in the centrifugal composites (see Fig. 21) (Forster *et al.*, 2003).

This technique is predominantly used for the manufacture of tubes and pipes for water supply lines, gas pipes, sewage pipes and rings, bushings, engine cylinder liners, pistons, street lamp posts, brake drums, etc. (Ebhotu *et al.*, 2016).

Across-sectional optical micrograph of a sample produced by centrifugal casting is shown in Fig. 22 (Rahimipour and Sobhani, 2013).

It shows that the sample separated into two main sections during the centrifugal casting process. One of them is largely devoid of particles when compared to the other region. The 6 mm diameter sample therefore displayed a depleted region between 3 and 6 mm, whereas the inner core showed a high concentration of particles. The inner region also displayed a gradient in concentration with the highest concentration found near the segregation boundary. This observation is due to the solidification starting on the mold-melt interface and that the lighter particles then migrates in the opposite direction of the applied centrifugal acceleration (force) field (Rahimipour and Sobhani, 2013). The result is a segregation boundary somewhere in the middle where further particle migration stops (Fig. 22).

Resultant microstructures of AMCs produced by the centrifugal casting route presented by Rajan *et al.* (2010) are displayed in Fig. 23. They observed that the outer periphery of the cylindrical casting has a SiC content of 40 vol% that then reduces to 27, 24, and 23 vol% at 1.5, 2, and 2.5 mm from the outer periphery. Fig. 23 shows that a gradual or smooth transition in concentration is seen in matrix alloy. This is due to the presence of a varying amount of eutectic liquid.

Kana *et al.* (2018) developed functionally graded NbC/high chromium white cast iron composites by centrifugal casting. The general microstructural evolution across the composite can be observed in the optical micrographs presented in Fig. 24.

In Fig. 24(a–c), large volume fractions of primary spherical NbC particles (dark gray) can be observed up to 8 mm from the outer periphery (referred to as the hard layer). Between 8 and 9.5 mm (Fig. 3(d) and (e)), there is an abrupt transition in microstructure and a sharp decrease in the number of primary NbC particles and therefore NbC volume fraction. The primary NbC particles present here tends

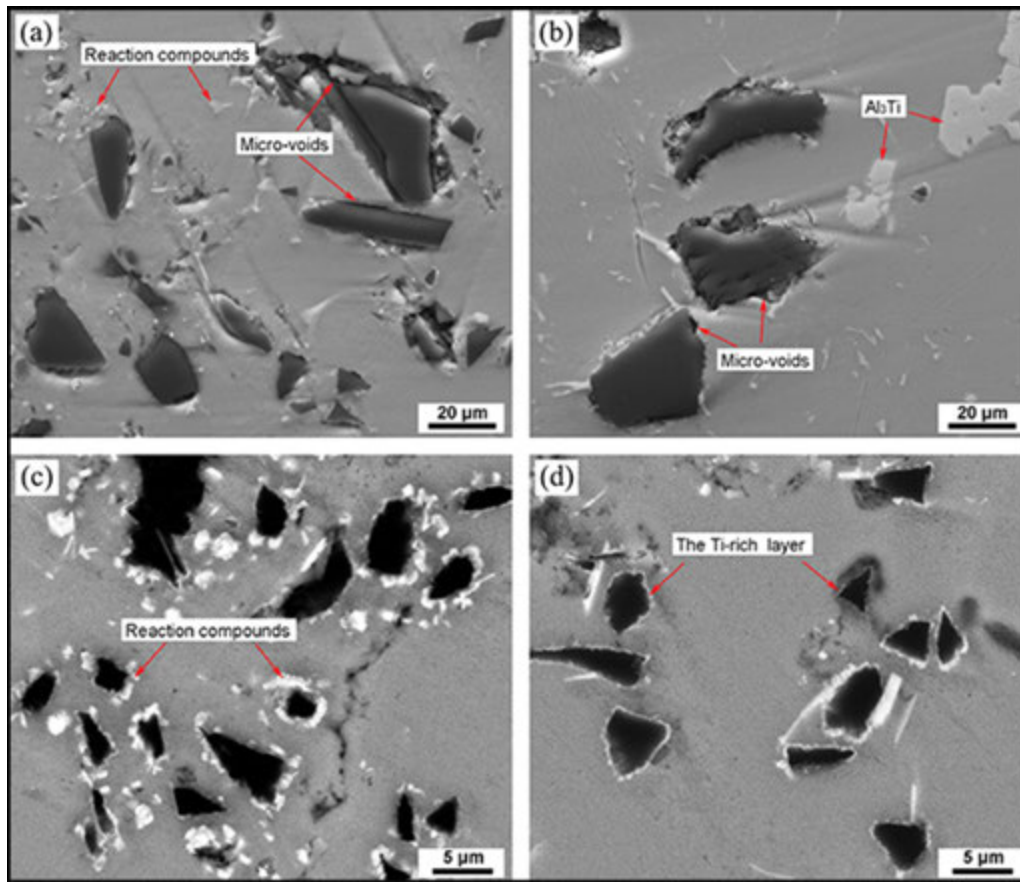


Fig. 17 SEM images of the microstructure of the A356–B₄C composites, fabricated by the semi-solid stir casting process: (a) S4 and (c) S6 without Ti additions; (b) S5 and (d) S7 with Ti additions. Reproduced from Hu, Q., Zhao, H., Li, F., 2016. Effects of manufacturing processes on microstructure and properties of Al/A356–B₄C composites. *Materials and Manufacturing Processes* 31, 1292–1300.

however to be significantly coarser and dendritic and is referred to as the transition region. NbC with a morphology resembling a eutectic phase (Filipovic *et al.*, 2013; Kesri and Durand-Charre, 1997; Haddad *et al.*, 2008), can also be observed. Porosity is however observed toward the innermost periphery, (Fig. 24(h)). This casting route is typically used only for tubular components for high pressure low volume fluid flow applications. Table 3 presents selected details regarding tensile behavior of different composites produced by centrifugal casting.

Squeeze Casting

Squeeze casting is the preferred metal matrix composite manufacturing process for a wide range of commercial applications because of the ability for of mass production, simpler process parameter control, improvements in wettability of the reinforcements by the liquid metal; better metallurgical quality of matrix alloys due to solidification under pressure and also has the ability to reinforce only selected regions of components. During squeeze casting, liquid metal is poured into a preheated die containing a preform (produced by powder metallurgy). Pressure is applied and solidifications occur under pressure. This minimizes porosity and produces near net shaped components which minimizes post processing operations (Chelladurai *et al.*, 2018; Vijian and Arunachalam, 2007; Senthil and Amirthagadeswaran, 2012; Girot *et al.*, 1990; Soundararajan *et al.*, 2016; Vijian and Arunachalam, 2006; Ghomashchi and Vikhrov, 2000; Samal and Newkirk, 2015).

Squeeze casting as utilized in general casting has also previously been referred to as extrusion casting, liquid pressing, pressure crystallization, and squeeze forming (Ghomashchi and Vikhrov, 2000). Fig. 25 presents a schematic setup of typical squeeze casting machine. In general, the process of squeeze casting involves the following steps (Ghomashchi and Vikhrov, 2000):

- (1) A pre-specified amount of molten metal is poured into a preheated die cavity that contains a preform, located on the bed of a hydraulic ram or press.
- (2) The press is activated to close off the die cavity and to pressurize the liquid metal. This is carried out very quickly, rendering solidification of the molten metal under pressure.

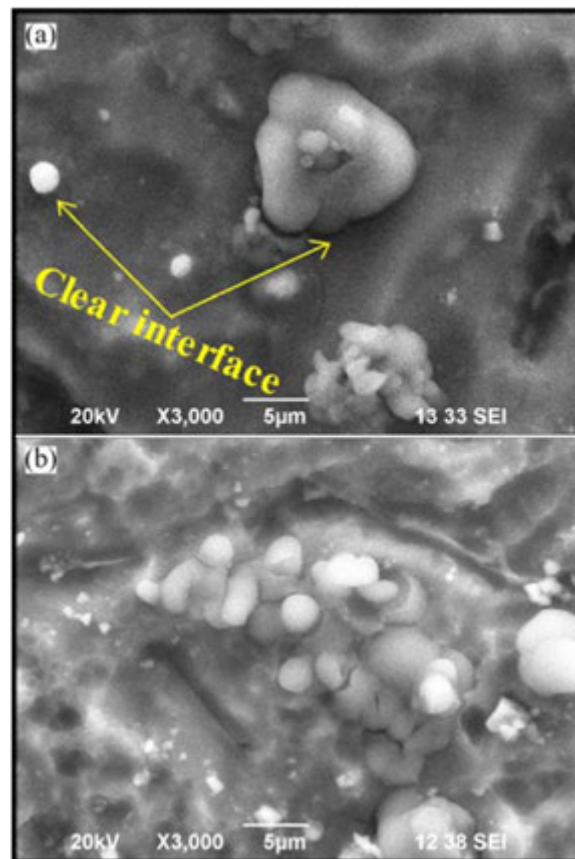


Fig. 18 SEM micrographs of AA6061/RHA AMCs with different amount of RHA at higher magnification: (a) 6%; (b) 8%. Reproduced from Allwyn Kingsly Gladston, J., Mohamed Sheriff, N., Dinaharan, I., David Raja Selvam, J., 2015. Production and characterization of rich husk ash particulate reinforced AA6061 aluminum alloy composites by compocasting. Transactions of Nonferrous Metals Society of China 25, 683–691.

Table 2 Tensile properties of selected AMCs produced by slurry casting

S.No.	Matrix	Reinforcement	Volume fraction	Size	Tensile strength (MPa)	Reference
1	A356	Al ₂ O ₃	3%.	50 nm	160	Sajjadi <i>et al.</i> (2012a)
2	A356	Al ₂ O ₃	1.8%	98.93 nm	278.24	Tofigh <i>et al.</i> (2015)
3	Al	SiC	10%	10 µm	344	Lin <i>et al.</i> (2010)
4	A356	B ₄ C	5%	32 µm	186	Zhang <i>et al.</i> (2014)
5	AA6061	fly ash	12%	1–2 µm	240	David Raja Selvam <i>et al.</i> (2013)
6	Al-Cu	SiCp	6.3%	60 nm	410	Qiu <i>et al.</i> (2017)
7	A356	SiCp		4 µm	265	Tzamtzis <i>et al.</i> (2009)
8	AA6061	Rice husk ash	8%	3 µm	245	Ghandvar <i>et al.</i> (2015)
9	AA7005	Al ₂ O ₃ p	10%		375	Ceschini <i>et al.</i> (2006)
10	A356	SiCp	20%	32–80 nm	105	Ghandvar <i>et al.</i> (2015)

- (3) The pressure is held on the metal until complete solidification. This not only increases the rate of heat flow, but also most importantly may eliminate macro/micro shrinkage porosity. In addition, since nucleation of gas porosity is pressure-dependent, the porosity formation due to dissolve gases in the molten metal is restricted.
- (4) Finally the punch is withdrawn, and the component is ejected. When including a preform during the manufacture of MMC's squeeze casting is also often referred to as the infiltration process.

This route is mainly used to make high volume fraction MMCs, and to overcome wettability problems (Feng *et al.*, 2008). The parameters that affect squeeze casting have been identified as: composition of the casting alloy, applied pressure level, die preheating temperature, pouring temperature, die coat material (lubricant), melt superheat, duration of pressure application, punch temperature, and delay time to achieve maximum pressure (Vijian and Arunachalam, 2007). Agglomeration, porosity, and

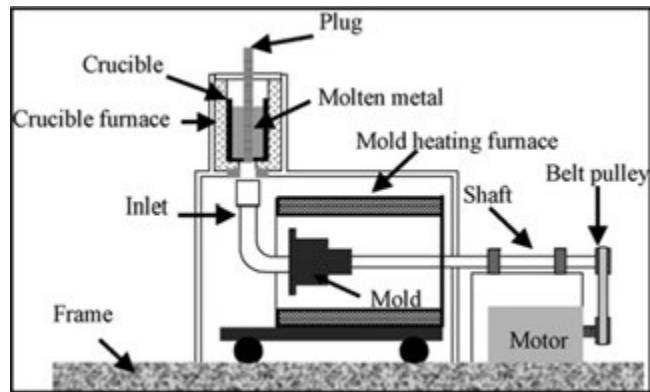


Fig. 19 Typical horizontal type centrifugal casting machine. Reproduced from Hadad, S.E., Sato, H., Watanabe, Y., 2010. Wear of Al/Al₃Zr functionally graded materials fabricated by centrifugal solid-particle method. *Journal of Materials Processing Technology* 210, 2245–2251.

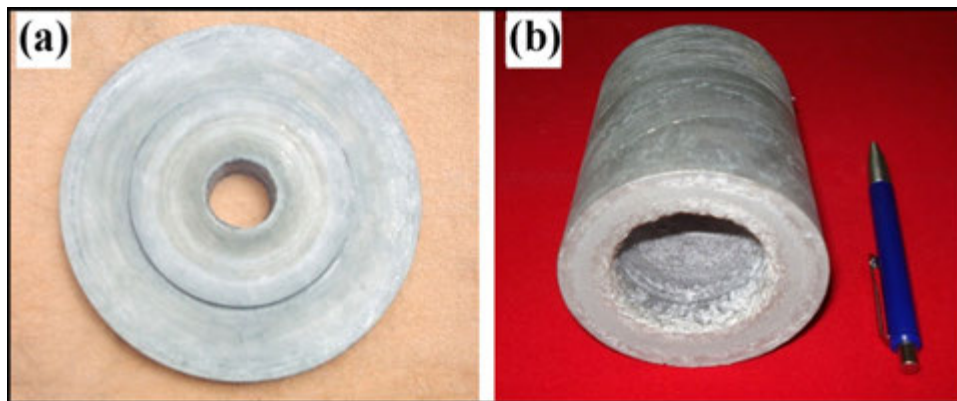


Fig. 20 A390/SiC functionally graded centrifugal cast; (a) brake rotor disc and (b) cylinder liner. Reproduced from Rajan, T.P.D., Pillai, R.M., Pai, B.C., 2008. Centrifugal casting of functionally graded aluminium matrix composite components. *International Journal of Cast Metals Research* 21, 214–218

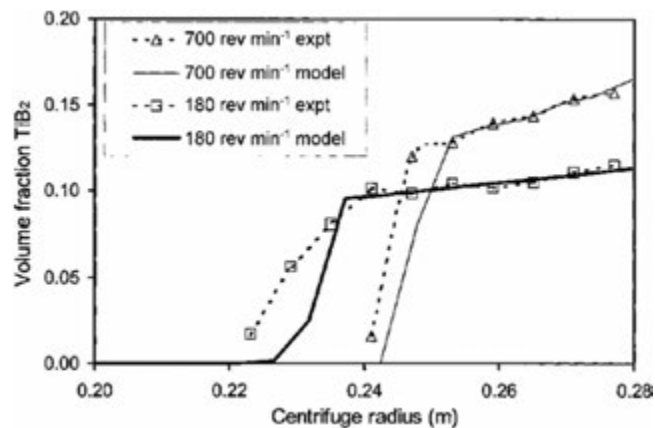


Fig. 21 Comparison of experimental results and model results of a centrifugally cast Al/TiB₂ composite. Reproduced from Forster, M.F., Hamilton, R.W., Dashwood, R.J., Lee, P.D., 2003. Centrifugal casting of aluminium containing in situ formed TiB₂. *Materials Science and Technology* 19, 1215–1219.

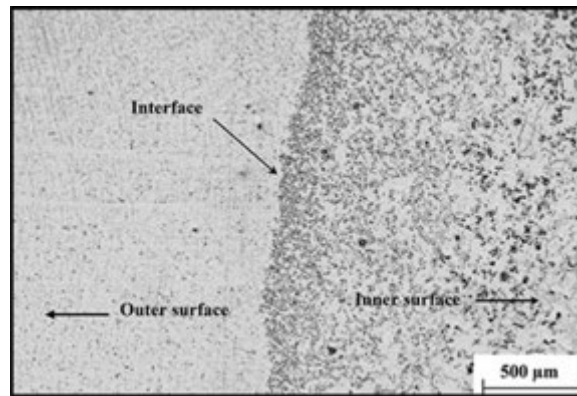


Fig. 22 Optical micrograph of particle migration due to centrifugal acceleration force in a gradient Fe-TiC composite. Reproduced from Rahimpour, M.R. and Sobhani, M., 2013. Evaluation of centrifugal casting process parameters for in situ fabricated functionally gradient Fe-TiC composite. *Metallurgical and Materials Transactions B* 44, 1120–1123.

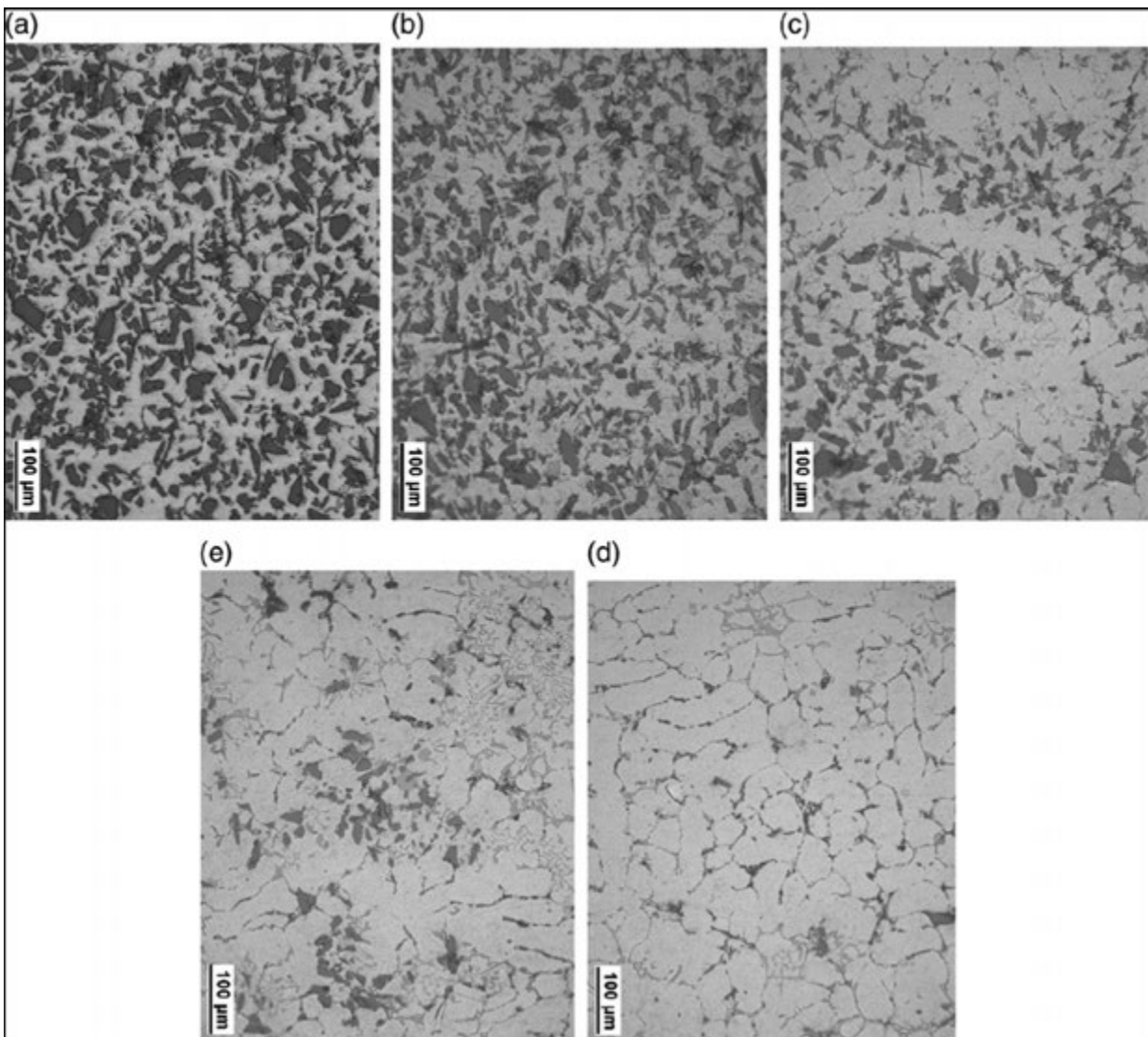


Fig. 23 Microstructures of Al (2124)-SiC FGMCC hollow cylinder fabricated by horizontal centrifugal casting. Microstructures are presented located from the outer periphery toward the inner periphery at different positions (in mm) [(a) 1 mm; (b) 1.5 mm; (c) 2.5 mm; (d) 5 mm; (e) 12.5 mm]. Reproduced from Rajan, T.P.D., Pillai, R.M., Pai, B.C., 2010. Characterization of centrifugal cast functionally graded aluminum-silicon carbide metal matrix composites. *Materials Characterization* 61, 923–928.

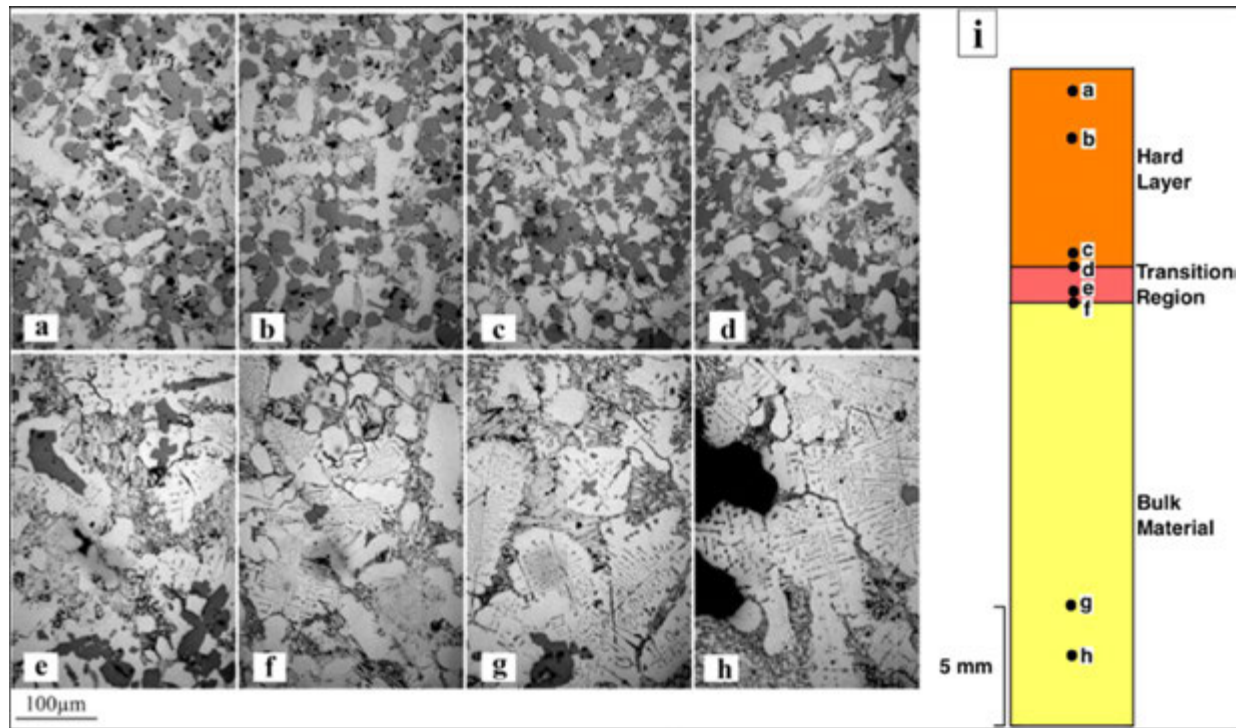


Fig. 24 Microstructure of a cast iron reinforced with NbC particles (dark gray)—distance from outer periphery: (a) 1 mm, (b) 3 mm, (c) 8 mm, (d) 8.5 mm, (e) 9.5 mm, (f) 10 mm, (g) 23 mm, (h) 25 mm, (i) schematic showing where the micrographs (a)–(h) were obtained from the casting. Reproduced from Kana, W.H., Albino, C., Costa, D.D., *et al.*, 2018. Microstructure characterisation and mechanical properties of a functionally graded NbC/high chromium white cast iron composite. *Materials Characterization* 136, 196–205.

Table 3 Tensile behavior of selected composites produced by centrifugal casting

S.No.	Matrix	Reinforcement	Volume fraction	Size	Tensile strength (MPa)	Reference
1	Al	SiC	15%	16 μm	146	El-Galy <i>et al.</i> , 2017
2	LM25 Al	Si ₃ N ₄	10%	40 μm	212	Radhika (2018)
3	Al	Al/TiB ₂	12%	10 μm	240	Radhika and Raghu, 2016
4	Al Alloy	SiC	41%	100 μm	260	Rajan <i>et al.</i> (2012)
5.	Al LM 25	WC	10%		156	Jojith and Radhika (2018)
6.	A356A2124	SiC	15%	12 μm	460	Sobczak and Drenchev, 2013
7.	A319	SiC	15%	23 μm	279	Jayakumar <i>et al.</i> (2016)
8.	7075 Al	SiC	6%	7–34 μm	223	Prabhu, 2017

wettability are the major issues that need to be controlled in this process. Typical applications for this casting route are in the automotive industry in producing aluminum front steering knuckles, chassis frames and brackets or nodes. Applications also include high capacity propellers for boat-engines.

Kalkanli and Yilmaz (2008) obtained a homogeneous distribution of the SiC particulates for production of Al 7075/SiC composites by squeeze casting. Fig. 26 presents the results of the SiC particle distribution in a 7075 alloy matrix. Minor agglomeration was observed but there was no evidence of porosity among the SiC particles even when they are in close proximity. This is evidence of the increased hydrogen gas solubility in the matrix during solidification under pressure.

Lu *et al.* (2018) prepared Al₂O₃/steel composites by squeeze casting. They found that the mechanical and metallurgical properties were improved by adding Si particles. Fig. 27 shows the microstructure comparison of the composites with and without Si powder in the preforms. For all the composites, the alumina particles are evenly distributed in the matrix along the infiltration direction of the steel melt. However, the volume fraction of alumina particles for the different composites varied. It varied between 43.35% and 58.34% as the Si content in the preforms changed 0%–25%. Initially a slight decrease from 43.35 to 41.47 was observed between 0%–15% Si where after a sudden rise to 58.34% was obtained between 20% and 25% Si.

The slight decrease in the Al₂O₃ fraction is due to some Al₂O₃ being replaced by the Si powder in the preforms. However, the sudden increase in the Al₂O₃ fraction at higher Si levels is more difficult to explain. It may be that the increased Si powder added in the preforms damaged the network of the Al₂O₃ so that the preforms collapsed, and that the Al₂O₃ particles were then displaced toward a closer proximity due to the infiltrating steel melt after Si powder was melted.

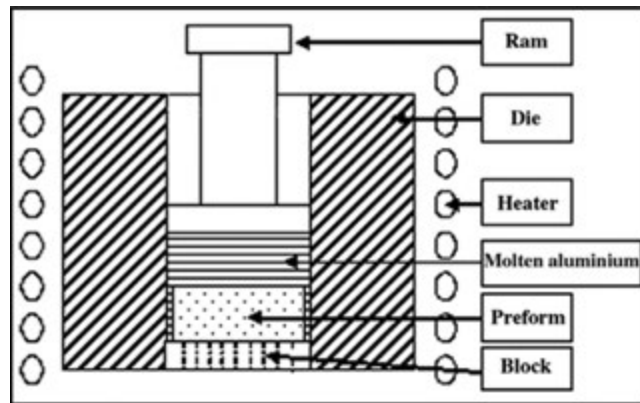


Fig. 25 Schematic diagram of a typical squeeze casting machine. Reproduced from Feng, Y.C., Geng, L., Zheng, P.Q., Zheng, Z.Z., Wang, G.S., 2008. Fabrication and characteristic of Al-based hybrid composite reinforced with tungsten oxide particle and aluminum borate whisker by squeeze casting. *Materials and Design* 29, 2023–2026.

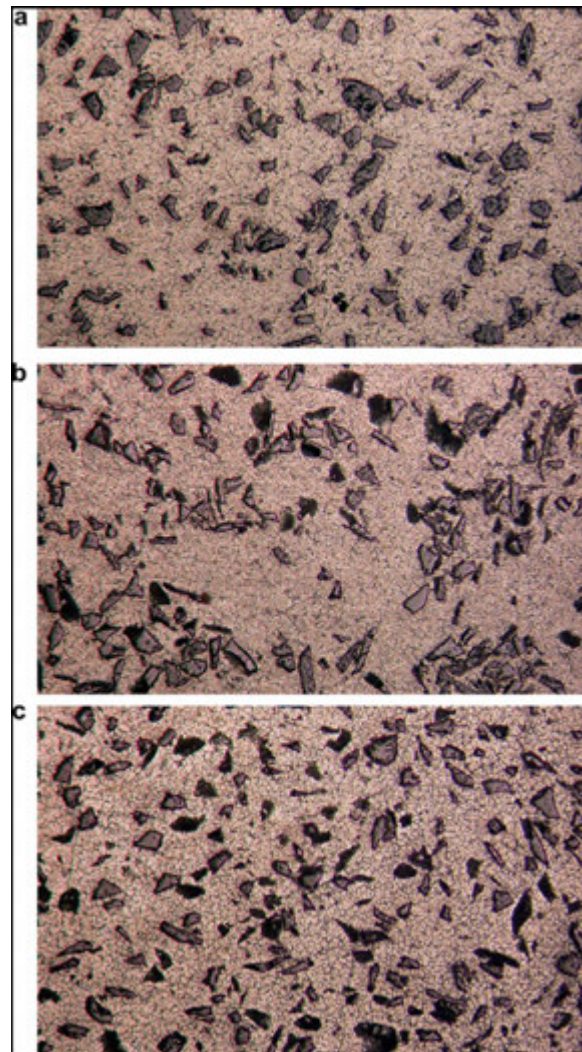


Fig. 26 Optical micrographs of (a) 10 wt%, (b) 15 wt%, (c) 20 wt% silicon carbide reinforced 7075 aluminum composites ($200\times$ magnification). Reproduced from Kalkanli, A., Yilmaz, S., 2008. Synthesis and characterization of aluminum alloy 7075 reinforced with silicon carbide particulates. *Materials and Design* 29, 775–780.

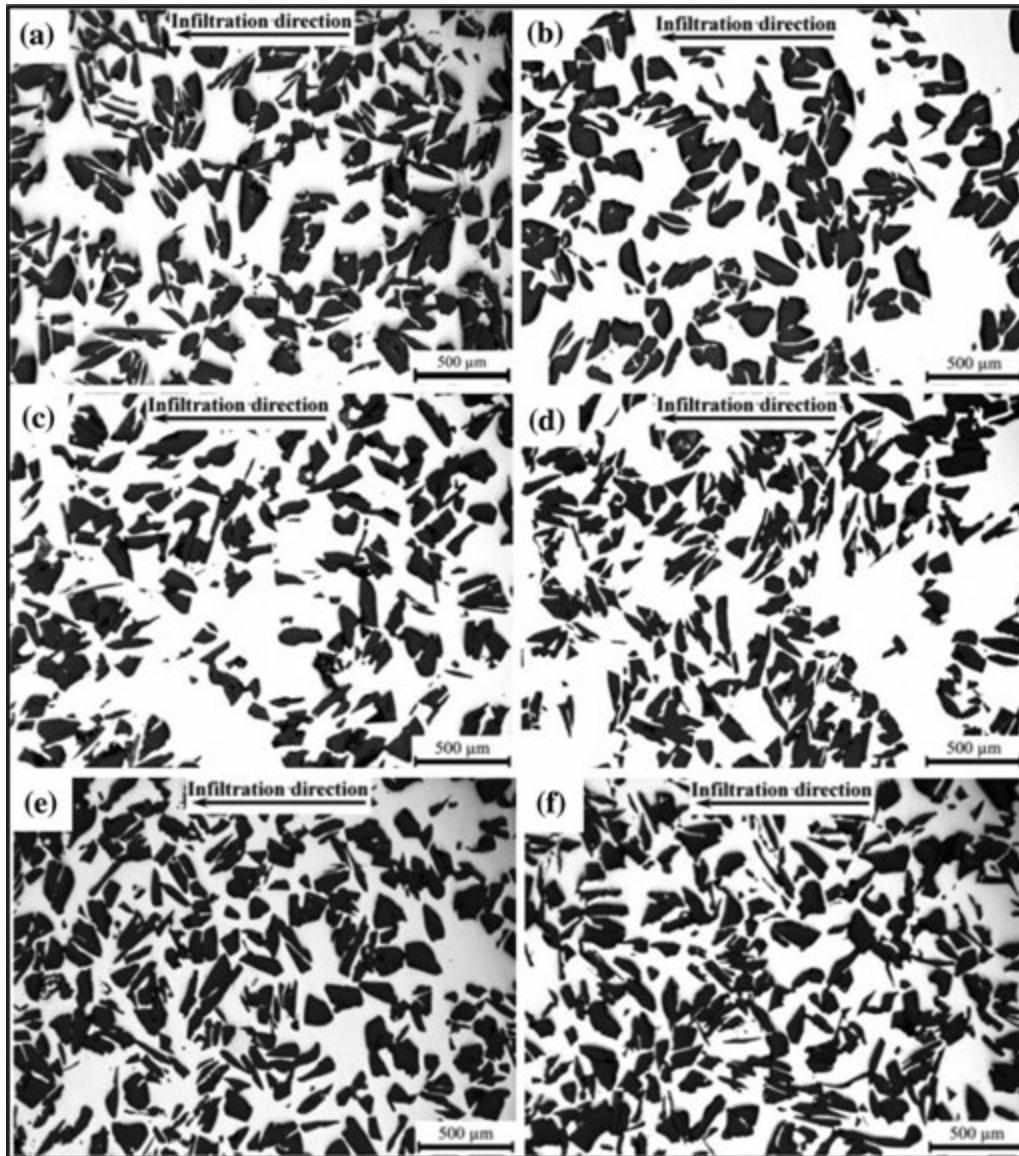


Fig. 27 Micrographs of Fe/Al₂O₃ composites without Si and with different Si powders in the preforms (unetched). (a) Without Si powder; (b) 5% Si powder; (c) 10% Si powder; (d) 15% Si powder; (e) 20% Si powder; (f) 25% Si powder. Reproduced from Lu, D.H., Li, H.Z., Ren, B., 2018. Effect of Si content on impact-abrasive wear resistance of Al₂O₃p/steel composites prepared by squeeze casting. *Journal of Iron and Steel Research International* 25, 984–994.

Kevorkijan (2004) prepared semi-industrial samples of Mg AZ80/SiC/50p composites successfully by pressure-less, low-pressure, and moderate-pressure infiltration.

Fig. 28 presents a typical optical micrograph showing SiC particulates in the AZ80 matrix obtained by moderate-pressure infiltration. This clearly demonstrates the merit of these infiltration routes in overcoming the segregation problem, which is one of the major drawbacks of the conventional casting routes for the production of composites. The main advantage of moderate-pressure infiltration is the superior productivity in comparison with infiltration under ambient pressure.

Chi *et al.* (2015) added (h-BN) particles to produce 2024Al/TiB₂ composites. SEM images of the TiB₂/2024Al and (TiB₂ + h-BN)/2024Al composites along with the associated EDXS analysis of the interface phase (point A in Fig. 29(b)) and a XRD spectrum of (TiB₂ + h-BN)/2024Al composite are shown in Fig. 29. The images show a largely homogeneous distribution of TiB₂ particles in both composites with limited agglomeration of TiB₂ particles in some locations of the TiB₂/2024Al composite. The distribution of h-BN is mostly homogenous.

In addition, an Al₂Cu phase is found in the composite located near the agglomerated TiB₂ particles. Point A (in red circle) is the position of EDXS analysis of Al₂Cu phase as shown in Fig. 29(c). From the results of the EDXS it can be seen that the main elements are Al and Cu, and that the atomic percentage ratio of the two elements is nearly 2:1. The presence of Al₂Cu is also further supported by the XRD results in Fig. 29(d).

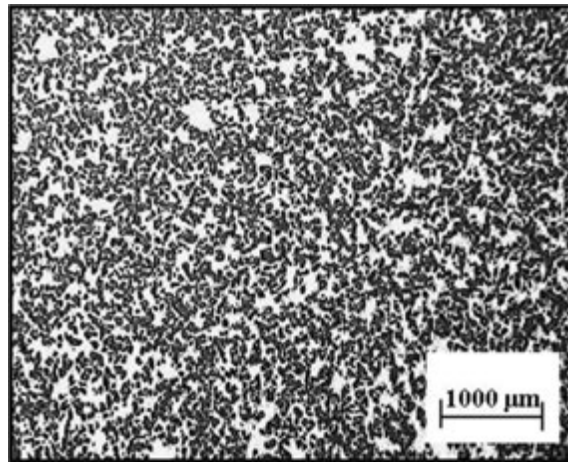


Fig. 28 SEM micrograph of void-free Mg AZ80/SiC/49.2_p composite obtained by moderate-pressure infiltration. Reproduced from Kevorkian, V., 2004. Mg AZ80/SiC composite bars fabricated by infiltration of porous ceramic preforms. *Metallurgical and Materials Transactions A* 35, 707–715.

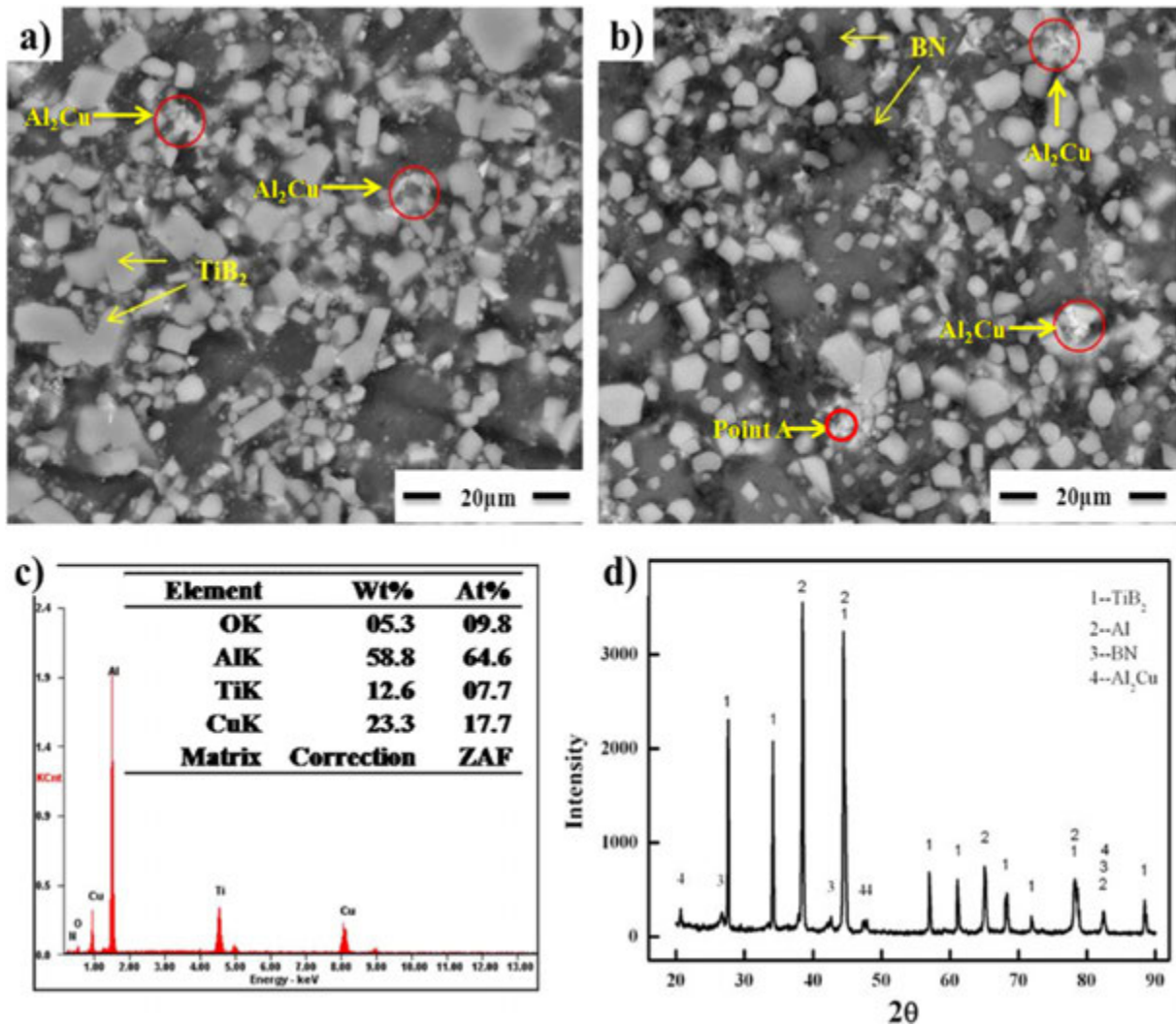


Fig. 29 (a) and (b) SEM images of (TiB₂ + h-BN)/2024Al composite; (c) XRD patterns of the composite; (d) EDXS result of the interface phase. Reproduced from Chi, H., Jiang, L., Chen, G., *et al.*, 2015. Dry sliding friction and wear behavior of (TiB₂ + h-BN)/2024Al composites. *Materials and Design* 87, 960–968.

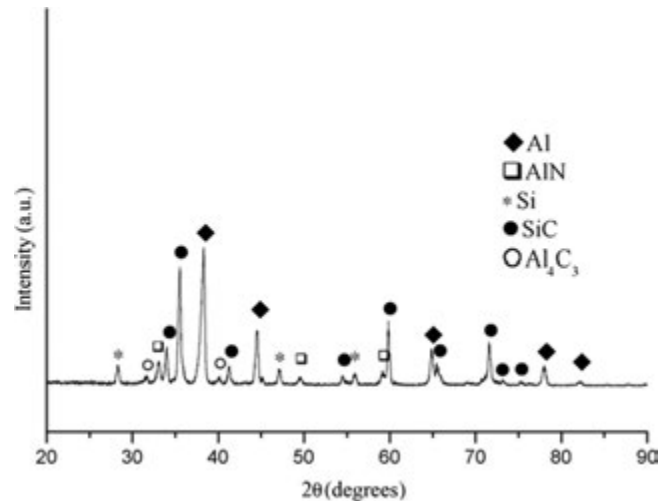


Fig. 30 XRD pattern of Al/SiC composite processed for 60 min with 9 wt% Mg in the alloy and GC-SiC/C-SiC ratio of 75/25. Reproduced from Celaya, F.O., Canul, M.I.P., Cuevas, J.L., Angeles, J.C.R., Canul, M.A.P., 2007. Microstructure and impact behavior of Al/SiCp composites fabricated by pressureless infiltration with different types of SiCp. *Journal of Materials Processing Technology* 183, 368–373.

Table 4 Tensile behavior of selected composites produced by squeeze casting

S.No.	Matrix	Reinforcement	Volume fraction %	Size	Tensile strength (MPa)	Reference
1	Aluminum	WO ₃ p + ABOw	3 + 22	18 + (0.5–1) μm	287.30	Feng <i>et al.</i> (2008)
2	LM6 alloy	Copper coated steel fiber	10	194 μm	164	Chelladurai <i>et al.</i> (2018) and Kalkanli and Yilmaz (2008)
3	7075Al	SiCp	45	5 μm	630	Xiu <i>et al.</i> (2015)
4	2024Al	Si ₃ N ₄ p	45	1.5 μm	360	Xiu <i>et al.</i> (2012)
5	Al	SiC	55–57		220	Yana <i>et al.</i> , 2008
6	LM6 alloy	Al ₂ O ₃	5	85 nm	230	Sevik and Kurnaz (2006)
7	Al	AlN	50	4 μm	360	Zhang <i>et al.</i> (2003)
8	Al7075	SiC	10	29 μm	340	Kalkanli and Yilmaz (2008)

Celaya *et al.* (2007) studied the effect of the Mg content (6% to 9%) in an aluminum composite alloy and the effect of holding time on the composites microstructure and impact strength. They observed that composites obtained with 9% Mg exhibit an average impact strength which is four times the strength of those processed with 6% Mg.

Fig. 30 Shows the XRD pattern of a composite processed for 60 min with 9 wt% Mg in the alloy. According to the XRD results, no evidence was found concerning the formation of other phases, such as Al₂O₃, MgO, or MgAl₂O₄, in addition to AlN. It is most likely that due to the presence of Mg in the alloy, spinel was produced.

Squeeze casting may exhibit the following limitations: brittle composite due to high volume fractions, interfacial reactions, die erosion, high capital cost, shortened die life, limited shape complexity, difficult to produce thin sections, and limited maximum size and weight (Ghomashchi and Vikhrov, 2000). Table 4 presents selected details about the tensile behavior of different composites produced by squeeze casting.

Summary and Future Outlook

The current article presented various casting routes for producing MMCs. These included stir casting, slurry casting, centrifugal casting, and squeeze casting. The basic technique, appropriate process parameters, advantages, and disadvantages are presented.

MMCs that utilize advanced reinforcements including Carbon Nano Tubes (CNT), Graphene and nano ceramic particles are increasingly gaining more attention due to the potential delivering exceptional mechanical and other physical properties. These may offer enormous potential for a wide range of applications (Xiu *et al.*, 2015). Until recently, CNTs were the dominant carbon nano fillers used in metal matrix composites (MMCs) with extensive research work demonstrating that CNTs can provide a high degree of reinforcement of both mechanical and functional properties (Xiu *et al.*, 2012). The most significant requirements of MMC fabrication utilizing CNT include matrix reinforcement, interfacial reaction and chemical stability of the reinforcement.

Other factors include (1) homogeneity of the CNT dispersion (2) chemical and structural stability (3) bonding strength between the CNT and matrix during MMC processing. The interfacial phenomena and chemical stability of the CNTs in the metal matrix are critical. Uniform dispersion of CNTs has been the main challenge in CNT-reinforced composites be they polymer, ceramic or metal matrix. Compared with CNTs, graphene is considered easier to disperse into the matrix, as well as potentially being more cost-effective (Xiu *et al.*, 2012). Technological challenges in processing graphene reinforced MMCs are driven mainly by the strong van der Waals forces between aromatic rings. Graphene is difficult to disperse uniformly into a metal matrix since it tends to form agglomerates in order to reduce its surface energy during processing (Xiu *et al.*, 2012). In addition, obtaining effective interfacial bonding is difficult due to the poor affinity of graphene to metals. Another challenge is that graphene can easily become damaged during the harsh fabrication conditions (i.e., high temperature and high pressure) usually employed to produce MMCs, weakening its intrinsic properties (Xiu *et al.*, 2012).

Researchers have also explored possibilities of utilizing microwave-based heating technology in melting or casting processes. The in-situ microwave casting of metallic materials is a recent development. The process works on the principles of hybrid microwave heating and is accomplished inside the applicator cavity. The process involves – melting of the charge, in-situ pouring and solidification of the melt. The electromagnetic and thermal properties of the charge affect microwave-material interaction and hence melting of the charge. On the other hand, cooling conditions inside the applicator controls the solidification process. Significant parameters (Yana *et al.*, 2008) affecting microwave heating include (1) dielectric and magnetic properties, (2) heating mechanisms, (3) load subjected to microwave heating, and (4) applicators used for heating the materials and other underlying factors that may influence these parameters.

Rambo *et al.* (2005) identified a novel route to produce a TiC reinforced metallic matrix composite with considerably reduced processing time by pressureless low temperature reactive infiltration of a TiCu alloy into porous carbon preforms. The preforms were produced by 3D-printing of a starch powder. Porous carbon preforms can be easily shaped in a large variety of complex macro and microstructures. This technique may replace the various casting route to produce MMCs.

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Powder Metallurgy Routes for Composite Materials Production

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Nomenclature

AFF	Accumulative fold forging	MMC	Metal matrix composite
BPR	Ball to powder weight ratio	ODS	Oxide dispersion strengthened
CIP	Cold isostatic pressing	PM	Powder metallurgy
CMC	Ceramic matrix composite	PMC	Polymer matrix composite
CNT	Carbon nanotube	SHS	Self propagating high temperature synthesis
FGM	Functionally graded material	SPD	Severe plastic deformation
HIP	Hot isostatic pressing	SPS	Spark plasma sintering
HP	Hot pressing	TD	Theoretical density
LPS	Liquid phase sintering	UFG	Ultra fine grained

Introduction

Modern technologies require materials with unusual combinations of properties that cannot be met by the conventional metals, alloys, ceramics and polymeric materials. This is especially true for materials that are used in critical applications like aerospace, high temperature, underwater/corrosive environments and transportation applications. For such applications, there is a need of special materials that exhibit better combinations of individual properties. A composite is that special material and considered to be a multiphase material that exhibits a significant proportion of the properties of both constituent phases and have distinct interface between the constituent phases. The composite materials constitute matrix and the reinforcement materials. The matrix phase is generally soft which holds the reinforcement materials, whereas reinforcements are hard and brittle phase. The matrix phase transfers the load from matrix to reinforcement, whereas reinforcement mainly bears the load of the composite. Depending on the nature of the matrix and reinforcement phase, composite materials are categorized as metal matrix composite (MMC), ceramic matrix composite (CMC) and polymer matrix composite (PMC). The reinforcement phase can be either particulate form or fiber form.

There are various fabrication methods available to manufacture the composite materials. Among them, powder metallurgy is unique manufacturing method as it has the ability to fabricate high quality, complex parts to close tolerances in an economical manner. Powder metallurgy is the study of the processing of metal powders, including the fabrication, characterization, and conversion of metal powders into useful engineering components. It is a flexible manufacturing process capable of delivering a wide range of new materials, microstructure and properties. Fig. 1 shows the conceptual flow chart for powder metallurgy from the powder through the processing to the final product.

The applications of powder metallurgy are versatile since unique property or microstructure can be achieved using P/M approaches. Some examples include porous materials, oxide dispersion strengthened alloys (ODS), cermet (ceramic-metal composites), cemented carbide and biomaterials. The manufacturing of reactive and refractory metals and amorphous or glassy metals are quite difficult to process by other techniques. Powder metallurgy is the only process by which these materials can be manufactured. This process wins the cost competitions on the basis of its lower energy consumption, higher material utilization and reduced number of process steps, in comparison with other production technologies. It is also possible to eliminate machining operations completely in PM processing but that step is essential in other conventional manufacturing processes. It also has the abilities to form complex geometrical shapes directly to hold close dimensional tolerance control in the sintered product. Fig. 2 shows the basic processes involved in powder metallurgy. The key steps include powder production, blending/mixing powder, compaction and sintering of compact.

Powder Manufacturing Methods

The formation of powder involves the delivery of energy to the material to create new surface area. There are four methods by which powders are prepared. The methods are-

- (1) Mechanical fabrication technique
 - (2) Electrolytic fabrication technique
 - (3) Chemical reduction technique
 - (4) Atomization technique
- (1) Mechanical fabrication technique – The four fundamental mechanical comminution methods: impactation, attritioning, shearing and compression are involved during fabrication of powder by mechanical fabrication technique. The basic comminution techniques used for powder production are-

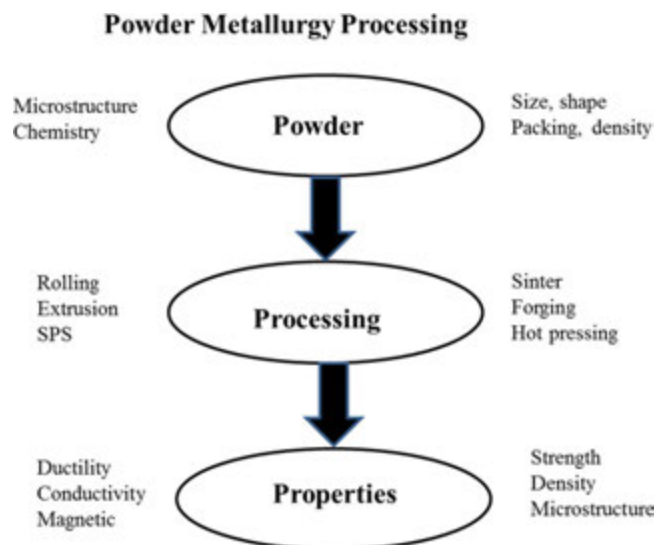


Fig. 1 The conceptual flow chart for powder metallurgy from the powder through the processing to the final product.

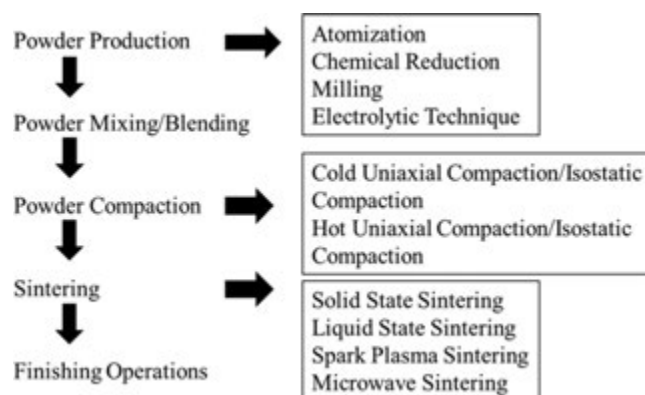


Fig. 2 Basic processes involved in powder metallurgy.

- (a) **Machining** – Machining of ingot during metal working processes generate powder. A large amount of scraps are generated and powder can be produced by grinding these scraps. The powder produced is coarse and lack of control on powder characteristics is major drawback of machining. Moreover, contamination of oxygen, oil and other metal is major disadvantage of machining technique for producing powder.
- (b) **Milling and Mechanical alloying** – Impacting and attritioning of powder/scraps using balls in a jar is another source of producing powder. During milling process, alloying of two or more elements can be done and is termed as mechanical alloying. Both milling/mechanical alloying is a complex phenomenon, as these involve with several parameters. The parameters are as follows:
 - (i) Milling speed
 - (ii) Ball to powder weight ratio (BPR)
 - (iii) Vial filling
 - (iv) Temperature of milling
 - (v) Milling atmosphere
 - (vi) Wet/dry grinding
 - (vii) Use of surfactant
 - (viii) Contamination problem

The details of the effect of milling parameters during grinding effect are available (Suryanarayana, 2001; Chaira and Karak, 2015). Ball mill, planetary mill, attritor mill, jar mill etc., are used as milling devices during milling and mechanical alloying. The contamination is a major problem in milling technique. The synthesis of powder not only depends on the various milling parameters

but also on the nature of material. The brittle materials are easily converted into powder by fracture, whereas ductile materials are initially plastically deformed. In later stage, ductile materials are work hardened, become brittle and finally fractured into powder.

- (2) Electrolytic fabrication technique – The raw metal is dissolved at the anode and deposited at the cathode in an electrolytic cell under certain operating conditions. The main advantage of this technique is ability to produce high purity powder. Powder formed by this technique is dendritic or sponge in shape, although particle size and shape can be controlled. The powders of Pd, Cu, Ni Z, Mn and Ag can be produced by this technique.
- (3) Chemical reduction technique – In this technique a metal oxide is reduced by reducing gases (CO, H₂) at suitable temperature and pressure and metal powder is produced. Oxides of Fe, W and Cu are reduced by reducing gases and powders are produced by this technique. The particles size and shape varies depending on the reduction parameters like gas composition, temperature, gas partial pressure and reaction kinetics. The powder produced by this technique generally exhibit poor flowability and packing characteristics.
- (4) Atomization technique – Powder is produced commercially and at very high rates as high as 400 kg/min. This technique involves the formation of powder from molten metals or alloys using a spray of droplets. Powder is produced by three atomization techniques-
 - (a) *Gas atomization* – high velocity gases (air, N₂, Ar or He) exit from a nozzle break up a molten metal stream into finely divided liquid droplets which finally solidify and form metal powder. The melt must be superheated over the melting temperature. The designs vary with metal feed mechanism, sophistication of the melting, collection chamber and gas atomization is categorized as horizontal and vertical gas atomization. The basis of gas atomization is to deliver energy from a rapidly expanding gas to the metal stream to form droplets. The gas atomization process has a large number of operating variables – gas type, gas pressure and velocity, melt temperature and viscosity as it enters the nozzle, metal/alloy type, metal feed rate. These parameters are adjusted to tailor powder characteristics for various uses. Powder produced by atomization is spherical in shape with wide size distribution and integrity of metal/alloy powder can be maintained if performed totally under inert atmosphere. Atomization technique is used to produce powder of Al, Ni, Mg, Co, Pd, Cu, Fe, Au, Sn, Zn and Be alloys. The detail of atomization process is available elsewhere (German, 1994; Upadhyay and Upadhyay, 2011).
 - (b) *Water atomization* – In water atomization, high pressure water jets are directed against molten metal/alloy stream, forcing disintegration and rapid solidification. This process is similar to gas atomization, only difference is rapid quenching and differing fluid behavior. Here, control of particle shape and size is difficult due to rapid cooling. Moreover, oxidation of powder particle is a major drawback. Powder of stainless steel, Cu, brass, bronze, tool steel, Co and Ni alloys, precious metals and low melting temperature metals (Pb, Sn and Zn alloys) are prepared by water atomization technique.
 - (c) *Centrifugal atomization* – Powder of reactive metals/alloys is produced by centrifugal atomization technique. In this process, centrifugal force throws off the molten metal as a fine spray which solidifies into a powder. Reactive metals or alloys like Zr, Ti and Ni superalloys are produced by centrifugal atomization using rotating electrode concept. The consumable electrode made from desired material is melted at its end by either plasma arc or stationery W electrode and rotates at very high velocity (up to 50,000 rpm). Centrifugal atomization is carried out either vacuum or inert atmosphere to prevent oxidation. The main advantage of centrifugal atomization is powder cleanliness, spherical shape with high packing density and good flowability and uniform particle size. The main disadvantages are low production rate, high equipment and processing cost.

Table 1 shows the comparison of three atomization techniques. The table compares the size, shape and morphology of the powder produced by three atomization techniques.

Basic Processes in Powder Metallurgy

Mixing/Blending of Powder

A composite powder particle has two or more phases present with variation of size, shape and density. Composite particles are assembled to generate unique flow, packing, homogeneity and sintering. Homogeneous mixture is required with controlled segregation to obtain optimum properties of final consolidated composite product. Hence, most metal/alloy composite mixtures are prepared by blending or mixing in rotating containers. The schematic diagrams of such mixing devices are shown in Fig. 3. The volume of powder in mixer determines the mixing efficiency. A powder volume of 20%–40% of the mixer capacity is usually optimal. The rotational speed of mixer also plays an important role in mixing and optimal mixing of powder occurs at 75% of critical speed.

Table 1 Comparison of atomization techniques

Process	Size range, μm	Particle shape	Size distribution	Cost
Gas atomization	15–300	Rounded, spherical	Moderate	Moderate
Water atomization	5–800	Irregular, nodular	Wide	Low
Centrifugal atomization	200–600	Spherical	Bimodal	High

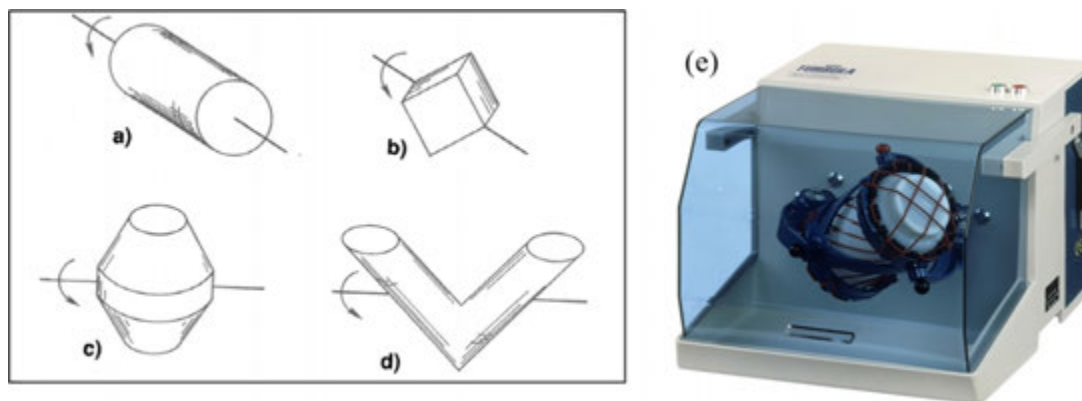


Fig. 3 Some common equipment used for mixing or blending powders: (a) rotating cylinders (b) rotating cube (c) double cone (d) twin shell and (e) Turbula shaker mixer T2F™. Reprinted with permission from German, R.M., 2005. Powder Metallurgy and Particulate Materials Processing. Princeton, NJ: Metal Powder Industries Federation, p. 173, Fig. 5.13. (d) German, R.M., 1994. Powder Metallurgy Science, second ed. Princeton, NJ: Metal Powder Industrial Federation.

Mixing with binders and lubricants

Mixing is the first step in the preparation of a powder-binder feedstock for shaping. Mixing is very crucial, since mixing deficiencies can not be corrected by subsequent processing. The inhomogeneties in a mixture occur in two main forms, separation of the binder from the powder and segregation according to particle size within the binder. The main aims in mixing are to coat the particles with binder, to break up agglomerates, and to attain uniform distribution of binder and particle size throughout the feedstock.

Friction between die wall and powder during compaction is a major problem. As the compaction pressure is increased, ejection of powder mass from the die becomes more difficult and lubricants are used to minimize die wear and ease ejection. Lubricants are usually mixed with metal/alloy powder as a final step before pressing. Usually stearate powders of Ca, Zn, Li, Mg and Al of 0.5–1.5 wt% are added with metal/alloy powder. During pressing, lubricants form a fluid that lowers friction by creating a thick film of high viscosity polymer. Low viscosity fluids are not effective since they will be forced away from the friction points by the high pressure used in powder compaction. It has been observed that flowability improves (flow time measured from hall flowmeter, 50 g sample) reduces with increasing lubricant content and ejection pressure decreases with increasing lubricant amount. It has also been found that the green density after compaction reaches maximum at 1 wt% of lubricant content and further addition of lubricant reduces green density (German, 1994).

Powder Compaction

After mixing the powder with lubricants and additives, the next step to be followed is compaction of powder. Loose powder particles can not be packed together more than tap density. To achieve higher density, external application of pressure is required. The rate of initial densification is high with application of pressure. As compaction proceeds, rate of densification decreases due to work hardening. As pressure is applied, initially rearrangement of particle takes place with filling of large pores giving a higher packing coordination. A sketch of the density versus compaction pressure during metal powder compaction, showing key stages and schematic of powder compaction are shown in Fig. 4(a) and (b) respectively.

During compaction, contact area and number of contacts increases with increasing pressure and also with progress of compaction. The point contacts undergo elastic deformation and at all contact points elastic energy is stored in the compact. High pressure increases density by contact enlargement through plastic deformation. As pressure increases, homogeneous plastic flow spreads from the contacts and entire particle becomes work hardened. Although strain hardening occurs in case of ductile materials, but in case of brittle materials densification occurs by fragmentation. The hardness and work hardening behavior both influence compaction. The particle size and shape also affect compaction behavior. Small particle size and irregular particle hinders compaction because of higher interparticle friction and higher particle work hardening rate.

Powder compaction techniques

Conventional compaction

Conventional compaction is carried out using cylindrical die and punches (upper and lower punches). In this technique, lower punch is placed inside the die and then powder is filled up. Then upper punch is placed at the top side of die. Finally, die and punch assembly is pressed under uniaxial compaction. Once pressure is applied for fixed time periods, upper punch is removed and the lower punch is used to eject the compact. Fig. 5 shows the schematic diagram of conventional die compaction. In conventional die compaction, when pressure is applied from top and bottom punches, the process is called double-action

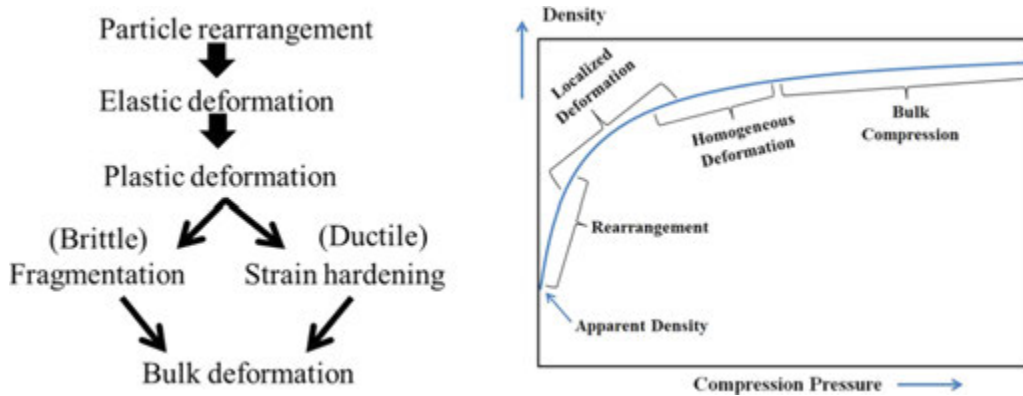


Fig. 4 (a) A sketch of the density versus compaction pressure during metal powder compaction, showing key stages and (b) schematic of powder compaction. Reproduced from (b) German, R.M., 1994. Powder Metallurgy Science, second ed. Princeton, NJ: Metal Powder Industrial Federation.

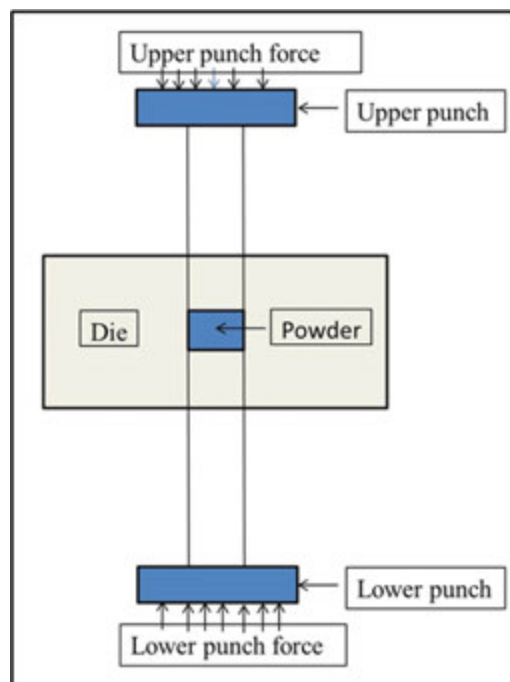


Fig. 5 Schematic of conventional die powder compaction.

pressing. On the other hand, when pressure is applied from only one punch, the process is called single action pressing. It can be shown that in case of single pressing, pressure at any position "x" below the punch as follows:

$$P_x = P \exp\left(-\frac{4uzx}{D}\right) \quad (1)$$

where D = Diameter of compact

P = Pressure applied at the top of punch

P_x = Transmitted pressure at the position "x" below the punch

z = Proportionality constant = radial stress/axial stress

The derivation of equation is available elsewhere (German, 1994). The equation shows that pressure decreases with depth in the powder bed. In uniaxial die compaction, pressure transmission decreases exponentially with height of compact. Hence, there is variation of pressure distribution along the length and radial cross section compact. The variation of pressure results in density gradient and it leads to variation in strength in the compact across the cross section. The height to diameter (H/D) ratio is

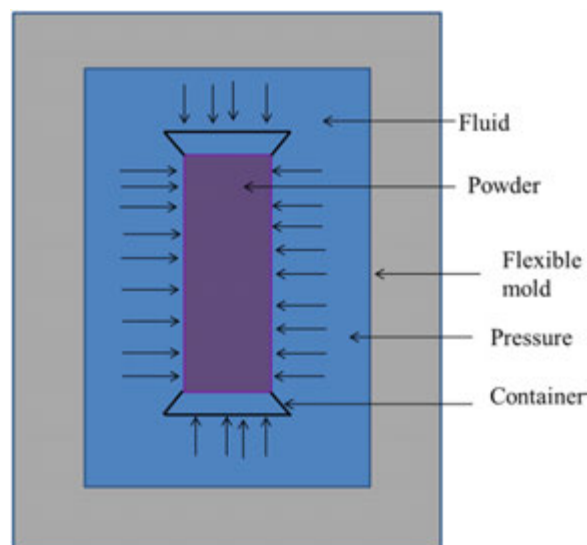


Fig. 6 Schematic diagram of cold isostatic compaction (CIP).

important to create uniform compact properties. Generally, when the height to diameter ratio exceeds five, die compaction is unsuccessful. To obtain uniform density and strength of compact, cold isostatic compaction (CIP) is adopted.

Cold isostatic pressing (CIP)

For complex shape, large length to diameter ratio and to achieve uniform density and strength, CIP is a viable technique. A flexible mold is filled with powder and pressurized isostatically using a fluid such as oil or water. As pressure is applied along all directions, higher density can be achieved as compared to conventional die compaction. Moreover, lower density gradients are achieved and complex shape can be compacted by cold isostatic pressing. **Fig. 6** shows the schematic diagram of CIP.

Sintering

Sintering is the bonding of particles at higher temperature. It can occur below the melting point (0.7–0.8 of melting temperature) by solid state sintering. Sintering also involves formation of liquid phase. The driving force of sintering is reduction in surface energy. Small particles have high surface area and sinter faster than coarse particle. Sintering is thermally activated process which occurs by atomic transport through diffusion.

Sintering mechanisms

Two types of transport mechanisms, surface transport and bulk transport occur in sintering. When sintering takes place between two particles, a neck is formed. In surface transport mechanism, no shrinkage or densification takes place, since mass originates and terminates at the surface. Surface diffusion and evaporation-condensation (EC) are two most important contributors during surface transport controlled sintering. Surface diffusion dominates during low temperature sintering of metals. On the other hand, bulk transport causes shrinkage or densification. The mass originates at the particle interior and deposits at the neck. Bulk transport mechanism includes volume diffusion, grain boundary diffusion, plastic flow and viscous flow. Although both surface and bulk transport processes gives neck growth, bulk shrinkage or densification occurs by bulk transport. Bulk transport generally occurs at high temperature. **Fig. 7** shows the schematic diagram of both bulk and surface transport.

Solid and liquid state sintering

Sintering can take place both in solid state or in liquid state. Surface energy is generally small driving force for solid state sintering. To obtain material with higher density and strength, sintering is more often enhanced. Sintering is enhanced by the formation of liquid phase, application of external stress (pressure assisted sintering), and addition of additives (activated sintering). In liquid phase sintering, a low melting phase is formed and this liquid phase may provide for rapid transport. There are certain criteria to be fulfilled for liquid phase sintering. These criteria are – (1) wetting is the first requirement. There should be good wettability between solid and liquid phase. Good wettability is fulfilled by low contact angle between solid and liquid phase, where liquid spreading will take place over solid surface. (2) The solid must be soluble in the liquid.

Sintering has a dominant role on the properties of P/M compacts. As the degree of sintering increases, the density, strength, ductility, thermal and electrical conductivity, corrosion resistance and other properties will improve. Sintering is a complex process which depends on several factors like sintering time, temperature, heating rate, sintering atmosphere and also on green compact.

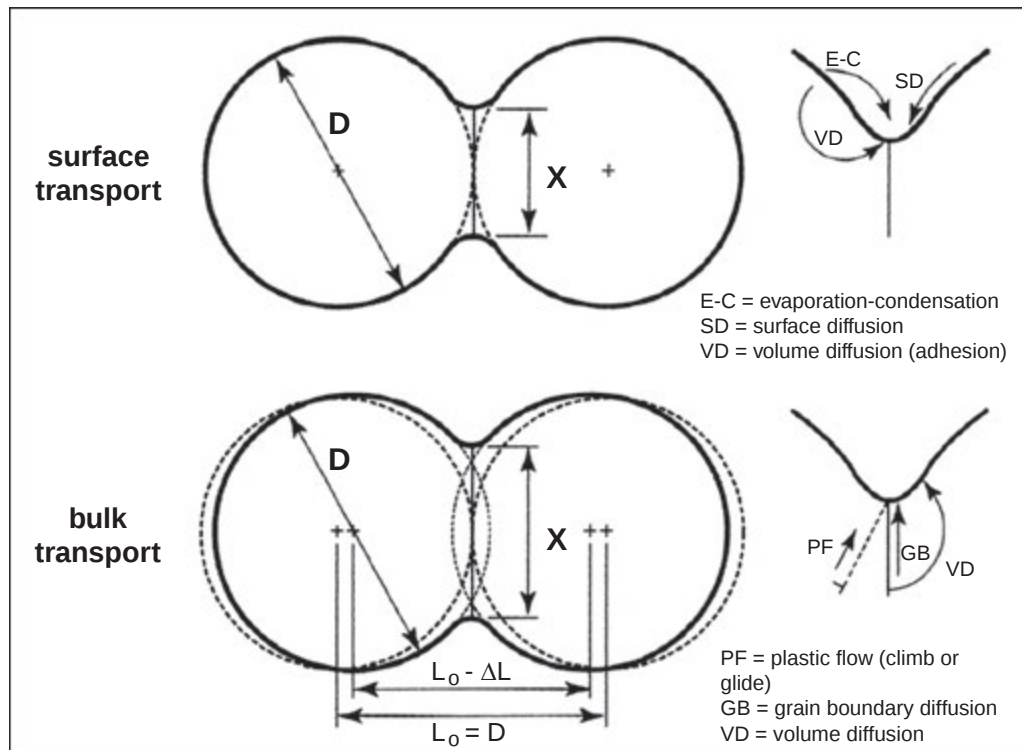


Fig. 7 Neck growth in sintering models for spheres of diameter D . The upper drawing shows neck growth measured by neck diameter X via surface transport mechanisms that do not produce shrinkage. The lower drawing is for bulk transport mechanism that move mass from between the particles to allow densification. Reproduced from German, R.M., 2014. *Sintering: From Empirical Observations to Scientific Principles*, first ed. United States: Elsevier-Butterworth Heinemann.

To obtain improved sintered properties, all the sintering parameters are to be optimized. Compaction at higher pressure gives higher strength, density, contact size and dimensional control after sintering. Higher compaction pressure leads to larger net neck sizes, however, compaction contributes at higher pressures.

Pore structure during sintering

The voids between particles generate pore in sintered product. After the initial stage of sintering, grain boundary and pore configuration control the sintering rate. At the beginning of intermediate stage, the pore geometry is highly convoluted and pores are located at grain boundary intersections. As sintering progresses, pore shape changes to cylindrical where densification occurs by reduction in pore radius. In the later stage of sintering, interaction between pore and grain boundary can take in three forms: the pore can retard grain growth, the pore can be dragged by the moving grain boundaries during grain growth or grain boundaries can break away from the pore, leaving them isolated inside the grain. At low temperature, pores remain attached with grain boundary and impede the movement of grain boundary. However, at higher temperature grain boundaries break away from the pores since pores are slower moving species than grain boundary. In the final stage of sintering, pores become spherical and isolated (German, 1994).

Fabrication of Composites by Powder Metallurgy

There are various methods by which composite materials can be fabricated. The fabrication methods depend on material system and properties requirement of the component. The methods can be broadly classified into two categories: conventional sintering methods and pressure assisted full density processing techniques. The conventional sintering method is followed after die compaction. The sintering technique is selected either solid state or liquid state sintering. On the other hand, in pressure assisted full density processing techniques, external pressure is applied. The techniques are-

- (1) Uniaxial hot pressing and hot isostatic pressing (HIP)
- (2) Spark plasma sintering
- (3) Microwave sintering

- (4) Powder forging
- (5) Powder rolling
- (6) Powder extrusion
- (7) Dynamic powder compaction

The various composite fabrication techniques using powder metallurgy are discussed below. Recent researches on fabrication of composites using powder metallurgy technique are also summarized.

Conventional Pressureless Sintering

The composite powder mixture is initially compacted by using die and then the compacted mass is sintered in furnace. During sintering, varieties of atmospheres like Ar, N₂, H₂, and NH₃ are chosen depending on materials system. The green compacts are sintered by solid state or liquid state. The rate of densification is lower in case of solid state sintering; hence sometimes external additives are added for formation liquid phase. The sintering temperature is generally 0.7–0.8 of melting point selected. The fabrication of various composites by researchers using compaction followed by pressureless sintering is highlighted below.

Gustafsson *et al.* (2008) fabricated Al₂O₃ + 5 vol% SiC composite by conventional pressureless sintering. They milled Al₂O₃ and SiC powder and then compacted CIP and pressureless sintered in a nitrogen atmosphere at 1750 and 1780°C. They obtained a full density of >99% at 1780°C. They achieved Vickers hardness and indentation fracture toughness of around 18 GPa and 2.3 MPa m^{1/2} respectively after sintering at 1780 °C and observed that addition of smaller additions of MgO promoted low temperature sintering. Xu *et al.* (2019) studied low-temperature preparation of Al₂O₃–ZrO₂ nanoceramics via pressureless sintering assisted by amorphous powders. They found that Al₂O₃–5 mol% ZrO₂ and Al₂O₃–10 mol% ZrO₂ were almost fully densified at temperature as low as 1350 °C and densification was attributed to the metastable state and phase transition of amorphous powders (Al₂O₃–ZrO₂), which acted as sintering aids. They also showed that the composites exhibited dense and homogenous mixture of Al₂O₃ and ZrO₂ particles with fine grain size, and the microstructure refinement further contributed to superior mechanical properties. Wang *et al.* (2019) studied pressureless sintering of B₄C with MoSi₂ (5–30 wt%) as a sintering aid carried out at 1600–2260°C in vacuum. They obtained relative density, fracture toughness and hardness of the samples with 30 wt% MoSi₂ sintered at 2260°C reach 96.5%, 3.98 MPa m^{1/2} and 28.1 GPa, respectively. They investigated that MoSi₂ can react with B₄C to in-situ form Mo₂B₅ and SiC below 1600 °C. It was also noticed that Mo₂B₅ gradually transform to MoB₂ with further increase in temperature. Bakhsh *et al.* (2013) fabricated carbon nanotube reinforced alumina nanocomposites by pressureless conventional sintering at 1600 °C under Ar gas. Their study showed that the densification can be achieved without degradation of carbon nanotubes at elevated temperatures in the carbon nanotube–alumina nanocomposites sintered by the conventional route. Bahaaddini *et al.* (2019) studied the effect of B₄C additive on pressureless sintering of LPS–SiC–Al₂O₃–Y₂O₃ composite. They observed that increasing the B₄C content up to 5 wt% enhanced the strength and fracture toughness of the composite samples, however increasing beyond 5 wt% led to a decrease in these properties. Li *et al.* (2013) fabricated SiC–BN composites with a BN content of 6 wt% by pressureless sintering at 2200 °C for 1 h and found to have 99.4% theoretical density and a high electrical resistivity of $1.24 \times 10^{10} \Omega \text{ cm}$. Liu *et al.* (2017) fabricated TiC–NiTi/Ni cermets by pressureless sintering at 1380°C for 1 h. They showed that the hardness and elastic modulus of the TiC0.7–NiTi cermets were lower than for the corresponding TiC0.95–Ni equivalent, whereas the fracture toughness and bending strength were significantly higher. They also observed that the Ni binder exhibited a brittle fracture, whereas the NiTi binder fractured in a ductile way. Mukhopadhyay *et al.* (2007) fabricated ZrO₂–30 vol% ZrB₂ composites by pressureless sintering in the temperature range of 1400–1600°C for 1 h in argon atmosphere. They studied the influence of yttria content in the zirconia matrix, as well as the sintering temperature, on the densification, microstructure and mechanical properties of the composites.

Uniaxial Hot Pressing and Hot Isostatic Pressing (HIP)

Uniaxial hot pressing is similar to die compaction where powder particles are consolidated generally in a graphite die using uniaxial pressing at high temperature. Fig. 8 shows the schematic diagram of uniaxial hot pressing. Here, compaction takes place by particle rearrangement and plastic flow (yielding at point contacts) followed by grain boundary and volume diffusion processes. The pressing is performed under inert atmosphere or vacuum to avoid contamination. One large commercial use for uniaxial hot pressing is in the consolidation of diamond-metal composite cutting tool.

The problem of uniaxial hot pressing is that the compact is not uniformly densified and hence uniform properties are not achieved. To obtain uniform properties of compact, hot isostatic pressing (HIP) is preferred. In HIP, flexible dies are used with isostatic pressurization. A deformable container is initially evacuated and degassed and then powder is filled. The consolidation of powder container is performed in an internally heated, cold-wall pressure vessel. High pressure gas, such as Ar or N₂ is sued to transfer pressure and heat for densification. The process is similar to CIP (Fig. 6), only difference is that HIP is performed at higher temperature but CIP is conducted at room temperature. This process is applied for the consolidation of many aerospace alloys like Ni base superalloys, Ti and Al alloys, composites and tool steel.

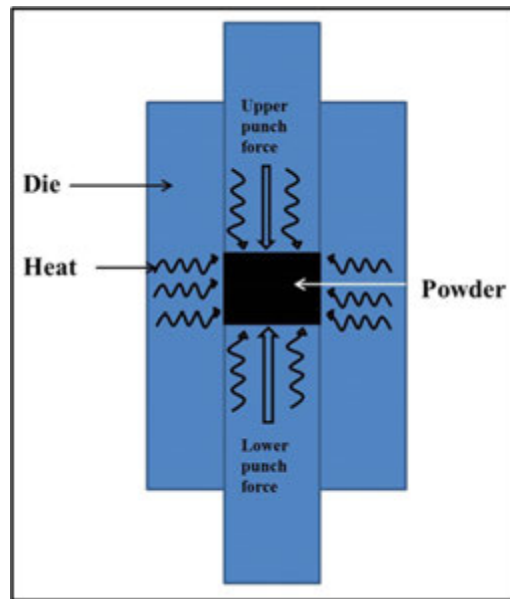


Fig. 8 Schematic diagram of uniaxial hot pressing.

Xu *et al.* (2015) fabricated Ti(C, N)-based cermets processed by both hot-pressing sintering and conventional pressureless sintering. They observed that pressureless sintering present higher transverse rupture strength, fracture toughness and density than samples fabricated by hot pressing. However, the hot pressed sintered samples possess a higher hardness. Canakci and Varol (2014) fabricated AA7075/Al-SiC composites using powder metallurgy and hot pressing. They observed that hot pressed density of the composites decreased with increasing amounts of Al powders and SiC content but hardness increased with increase of SiC content. Akbarpour and Pouresmaeil (2018) fabricated Al-CNT composite by powder metallurgy and hot pressing technique. They found that the increase of carbon nanotubes at 2 and 4 vol% increased the yield strength and compressive strength from 176 MPa and 201–241 MPa and 251 MPa and reduced the fracture strain from >20% to 4%, respectively. Gao *et al.* (2019) fabricated B₄Cp/6061Al composite by powder metallurgy followed by hot pressing in the temperature range of 560–600°C. They observed that density, yield strength and failure strain of the composites increased with increasing temperature from 560 to 600°C.

Spark Plasma Sintering (SPS)

Spark plasma sintering is best suited for consolidation of nanoparticles or ultrafine powder, where high amperage DC pulses current (1000 A) is passed through graphite die and powder mass. Low voltage of 5–10 V is applied through graphite die and punches. Heating rate as high as 500–600K/min can be achieved, where sintering can be performed within 5–6 min with full density, minimizes the chances of grain coarsening during sintering. The heat generation is internal, in contrast to conventional hot pressing, where heat is provided by external heating elements. When spark discharge appears in the gap between the particles, a local high temperature state occurs. This causes vaporization and melting of the surfaces of powder particles and necks are formed around the contact area between the particles during SPS process. Fig. 9 shows the schematic diagram of SPS process. There are certain advantages of SPS process than other conventional and pressure assisted sintering process. The advantages are:

- (1) Reduced sintering time
- (2) Good grain to grain bonding
- (3) Clean grain boundaries
- (4) Initial activation of powders by pulsed voltage
- (5) Resistance sintering under pressure.

The various composites fabricated by SPS are summarized below. Leszczyńska-Madej *et al.* (2019) fabricated Al-SiC composites reinforced with 10, 20 and 30 wt% SiC by SPS process at 580 and 600°C. They did not observe remarkable difference in the microstructure of the composites reinforced with SiC particles sintered at 580°C and 600°C. They found that the microstructure of the sintered compacts consists of uniform grains, the SiC strengthening phase particles locate on the grain boundaries. The use of a higher sintering temperature had a positive effect on hardness and the bending strength of the tested materials. Sayyadi-Shahraki *et al.* (2019) studied densification and mechanical properties of spark plasma sintered Si₃N₄/ZrO₂ nano-composites consolidated at 1600 °C under the pressure of 30 MPa for 10 min. They found that the addition of Y₂O₃-doped ZrO₂ into the initial Si₃N₄ powder can noticeably facilitate densification process, decreasing sintering temperature of

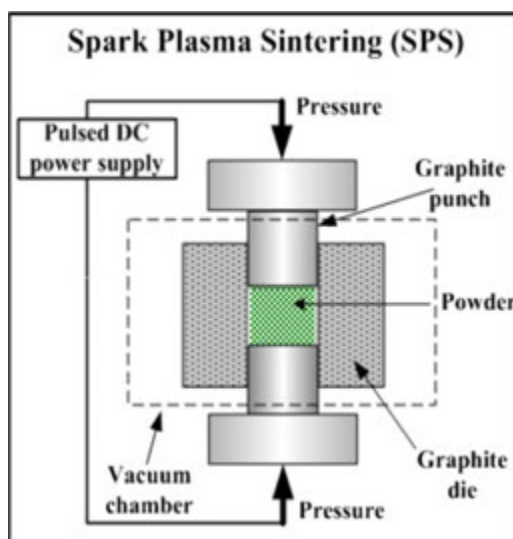


Fig. 9 Schematic diagram of spark plasma sintering (SPS). Available at: <https://www.substech.com>.

monolithic Si_3N_4 ceramic from 1600 to 1420°C through 30 vol% YSZ utilization. The study indicated that the hardness of the Si_3N_4 -base composites declined from 16.6 to 13.2 GPa, whereas the fracture toughness improved from 5.8 to 7.1 $\text{MPa m}^{1/2}$ by increasing ZrO_2 content from 0 to 30 vol%. Kgoete *et al.* (2019) studied oxidation resistance of Ti6Al4V-TiN composites fabricated by spark plasma sintering at 1000 °C for 6 min at 50 MPa pressure. They showed that the reinforced Ti6Al4V with TiN significantly improved the oxidation resistance, and hardness of Ti6Al4V alloy which is compactable and beneficial for aerospace application. They also observed that Ti-6Al-4V alloy reinforced with 5 wt% TiN yielded better results, with improved hardness value of 881.15 HV and less weight gain which indicates high temperature oxidation resistance. Akhlaghi *et al.* (2018) fabricated TiAl-Ti₃AlC₂ composite by spark plasma sintering at 1000°C for a dwell time of 15 min under an external pressure of 40 MPa in vacuum atmosphere. They achieved relative density of ~95%, Vickers hardness of ~4.5 GPa, fracture toughness of 11.9 $\text{MPa m}^{1/2}$, and flexural strength of 336 MPa. Mallik *et al.* (2019) studied spark plasma sintering of Ti-diamond composites, where they varied diamond content from 5 to 50 wt%. Sahani *et al.* (2016a,b) fabricated SiC-B₄C-Si and SiC-B₄C-Al cermets by both pressureless and spark plasma sintering techniques and observed that SPS is more efficient densification method than conventional pressureless sintering.

Microwave Sintering

Microwaves are electromagnetic radiation with wavelengths ranges from 1 mm to 1 m in free space and frequency varies from 300 GHz to 300 MHz respectively. It has been reported that microwave frequency of 2.45 GHz can be used for sintering of metal and ceramic powder (Roy *et al.*, 1999). Fig. 10 shows the schematic diagram of basic components of microwave sintering. In microwave sintering, heating is internal, uniform and high heating rate can be obtained as compared to conventional sintering.

Recent researches on fabrication of composites by microwave sintering are presented below. Mondal *et al.* (2013) studied the sinterability of the W-Cu system consolidated in a 2.45 GHz multimode microwave furnace and also critically compared with that processed in a radiatively heated (conventional) furnace. They found that microwave processing results in greater densification, more homogenous distribution of the binder phase, smaller tungsten grain size, higher electrical conductivity and hardness as compared to conventional sintering. Hong *et al.* (2019) fabricated $\text{Al}_2\text{O}_3/\text{SiC}$ composite ceramic tool material by two step microwave sintering (first step temp. varies from 1600 to 1700 °C and second step temp. 1100 °C) and compared with single step sintering (1600°C). They achieved relative density, grain size, Vickers hardness and fracture toughness of 98.37%, $0.78 \pm 0.31 \mu\text{m}$, $18.40 \pm 0.24 \text{ GPa}$ and $4.97 \pm 0.30 \text{ MPa m}^{1/2}$, respectively for the composite processed by two step and higher than single step sintering. Reddy *et al.* (2016) investigated structural and mechanical properties of microwave sintered Al-Ni₅₀Ti₅₀ composites. Duan *et al.* (2019) studied the effect of CNTs content on the microstructures and properties of CNTs/Cu composite fabricated by microwave sintering followed by rolling. They found that electrical conductivity and relative density of microwave sintered CNTs/Cu composites decreased with increase in CNTs content. It was also noticed that microwave sintering and subsequent rolling process enables better microstructure and performance of sintered composites which shows tensile strength of 218 MPa, the elongation of 37.75%, and the electrical conductivity of >98% IACS compared to pure copper. Ghasali *et al.* (2019) studied corrosion behavior and in-vitro bioactivity of porous Mg/ Al_2O_3 and Mg/ Si_3N_4 metal matrix composites fabricated by using microwave sintering process. They performed

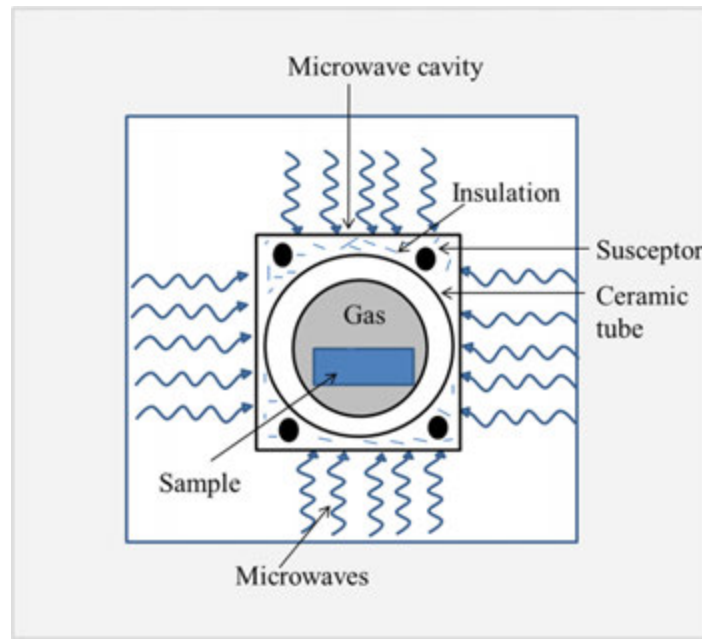


Fig. 10 Schematic diagram showing main components of microwave sintering process. Reproduced from Agrawal, D., 2013. Microwave Sintering of Metal Powders. United States: Woodhead Publishing Limited. Pennsylvania State University.

microwave sintering at 650°C without soaking time in a graphite bed and porosity of about 50% was measured for both sintered composites. Yang *et al.* (2019) studied flexural modulus of SiC/SiC composites sintered by microwave and conventional heating in the temperature range of 800–1100°C. They found that microwave heating led to much lower flexural modulus of SiC/SiC composites than conventional heating at the same sintering temperature.

Powder Rolling

In powder rolling, loose powder is gravity fed into the gap between two rolls which generate green sheet. The green sheet is then continuously sintered and rolled to obtain a full density strip product. Fig. 11 shows the schematic diagram of powder rolling process. Powder rolling is employed to fabricate sheet products of iron, copper, aluminum, nickel, steel, stainless steel, Mo–Cu, NiTi, Co–Fe, Cu–Pb and composites for applications ranging from battery electrodes to wear surface. Good compressibility is required to ensure that sufficient particle interlocking to give adequate green strip strength. The thickness of the finished strip and particle segregation restricts the maximum particle size which can be tolerated in the powder feed to the compaction mill. The powder must have flow smoothly and quickly through hopper with minimum tendency to stick slip or bridging.

The green strip thickness after powder rolling is calculated from the Eq. (2)

$$h_g = \frac{D(1 - \cos\alpha)}{C - 1} \quad (2)$$

where h_g is green strip thickness

D -roll diameter

α -angle of nip

C -compression ratio

From the above Eq. (2) it is found that strip thickness largely depends on roll diameter (D). Roll diameter of between 50 and 150 times the strip thickness are often required. The maximum strip thickness can be increased by increasing the ' μ ' i.e., by roughening the rolling surface. If the air entrapped in the powder is not properly released, the strip produced will not be of uniform density (Upadhyay, 1998).

Mo *et al.* (2015) studied the densification process of 10% B₄C–AA2024 matrix composite strips by semi-solid powder rolling. The gas atomized AA2024 and B₄C powders were initially preheated at 300°C. Then the mixed powders were firstly heated to 550, 585, 605, 625°C, respectively and held for 30 min and then fed into the gap to produce strips with a width of 100 mm and a thickness of 2.5–3 mm. They found that when the liquid phase is lower than 20%, rolling deformation is the main densification mechanism in deformation area. When the liquid fraction is higher than 20%, the flowing and filling of liquid are the densification mechanisms. Liu *et al.* (2014) also investigated microstructure evolution during semi-solid powder rolling and post-treatment of 7050 aluminum alloy strips. They showed that the best liquid fraction to prepare a strip ranges from 45% to 65%.

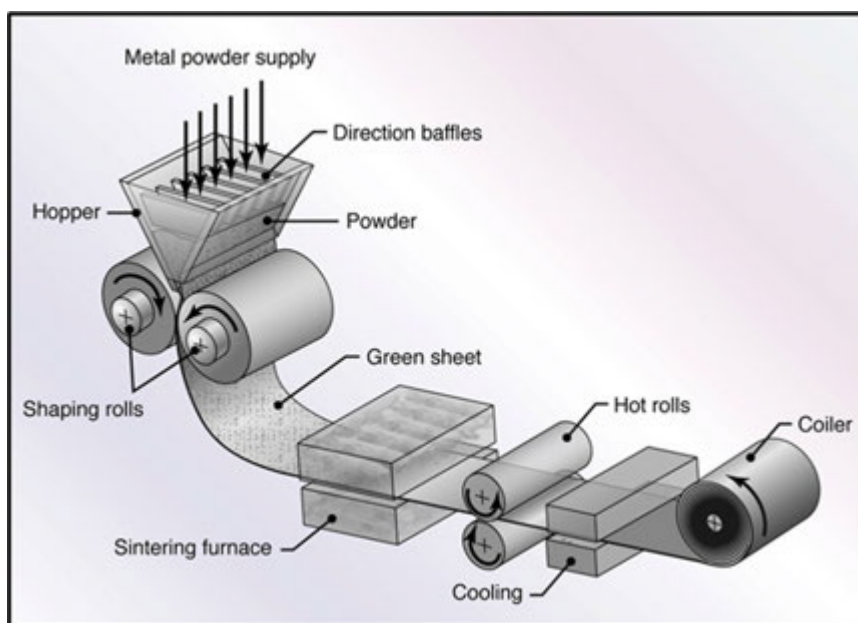


Fig. 11 Schematic diagram of powder rolling process. Reprinted with permission from German, R.M., 2005. Powder Metallurgy and Particulate Materials Processing. Princeton, NJ: Metal Powder Industries Federation, p. 330, Fig. 8.31. German, R.M., 1994. Powder Metallurgy Science, second ed. Princeton, NJ: Metal Powder Industrial Federation.

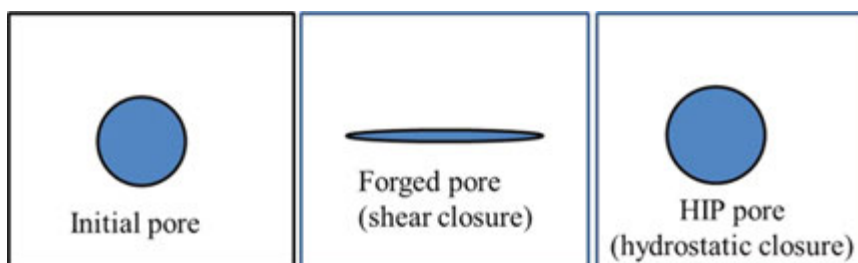


Fig. 12 Schematic diagram showing initial pore, pore in powder forging and in HIP process respectively.

They found that flowing and filling of liquid ($>10\%$), densification by rolling and recrystallization ($<10\%$) are the three combination mechanisms of the semi-solid powders during rolling.

Powder Forging

Powder forging is a high strain rate deformation process, typically conducted at elevated temperature, where material has a low strength and ductility. Conventional powder forging begins with custom-blended metal powders being fed into a die, then being compacted into a 'green' shape, which is then ejected from the die. The compact, called a 'preform' is different from the shape of final part will acquire after being forged. Again as in the conventional PM process, the green compact is sintered by solid state diffusion at a temperature below the melting point of the base metal in a controlled atmosphere furnace, creating metallurgical bonds between the powder particles and imparting mechanical strength to the preform. The heated preform is withdrawn from the furnace, coated with lubricant, and transferred to a forging press. Forging causes plastic flow, thus reshaping the preform to its final configuration and densifying it. Powder forging requires less handling, fewer dies and process steps as compared to conventional forging. Conventional forging of cast material require several steps to convert a billet into the final shape. But the parts fabricated by powder forging require only minor secondary machining and offer greater dimensional precision.

Powder forging is a combination of densification and flow under uniaxial forces. The pore collapse in forging is different from that encountered under hydrostatic condition used in HIP. Fig. 12 shows the schematic diagram of pore closure in powder forging and HIP process. The pore experiences higher shear in forging than in isostatic compaction. The difference in pore collapse contributes to more shear and bonding in powder forging. Powder forging is extensively used to fabricate various automobile components like connecting rods, cams, bearing races, off-road equipment and power tools.

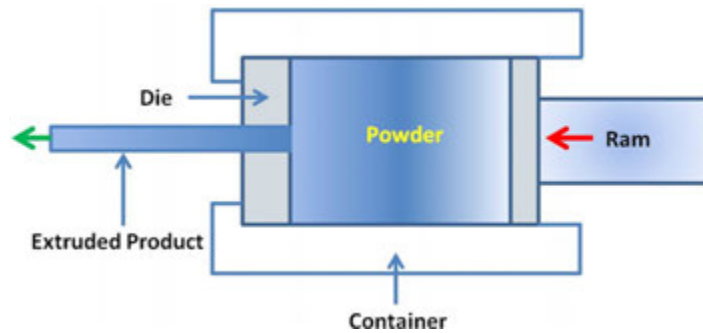


Fig. 13 Schematic diagram of powder extrusion process.

Khodabakhshi *et al.* (2019) fabricated AA8006-B₄C nanostructured nanocomposite by accumulative fold forging process (AFF), novel SPD process involves repetitive folding and forging steps with or without the incorporation of large fractions of nanoparticles between aluminum foil layers. They showed the uniform dispersion of the nanoparticles with less clustering/aggregation, low fraction of porosity, and strong bonding between the layers. They showed the refining of grain structure of aluminum matrix down to UFG range of ~200 nm and nano-sized range of ~35 nm with and without the B₄C nanoparticles and also improvement of modulus and hardness. Ozerov *et al.* (2019) investigated evolution of microstructure and mechanical properties of Ti/TiB metal-matrix composite produced by spark plasma sintering (SPS) at 1000°C using a Ti-10 wt%TiB₂ powder mixture and then subjected to multiaxial isothermal forging at 700 or 850 °C and a strain rate 10⁻³ s⁻¹. They found a considerable increase in low-temperature tensile ductility without substantial loss in strength. Qiu *et al.* (2012) fabricated Ti alloy connecting rod by powder forging technique and studied microstructure and mechanical properties. Alshammari *et al.* (2019) fabricated Ti-Mn alloys for biomedical applications by powder metallurgy using powder forging. They showed that Ti-Mn alloys have mechanical properties comparable to other Ti alloys commonly used in biomedicine such as Ti-6Al-4V or alloys being developed for dental and biomedical application such as other Ti-Mn alloy. Kumar *et al.* (2017) fabricated oxide dispersion strengthened (ODS) steels containing Fe-18% Cr-2%W-0.2%Ti with 0, 0.35, 0.5, 1 and 1.5% Y₂O₃ for future nuclear reactors. The elemental powders were mechanically alloyed and then the powders were placed in a mild steel can and forged in a stream of hydrogen gas at 1473K. They showed that the strength of ODS steel increased with yttria content accompanied by a decrease in tensile elongation.

Powder Extrusion

Powder extrusion is useful for fabricating high temperature alloys like oxide dispersion strengthened Cu, Al and Ni base superalloys. Long shapes with a constant cross section are the main products of extrusion. Extrusion involves relatively low temperature; hence a high level of shear is required for densification. For certain alloys and composites, the combination of temperature and shear proves optimal with respect to microstructure control and final properties. The schematic diagram of powder extrusion process is shown in Fig. 13.

The triaxial stress system set up in all three powder metal working processes. All three processes are related to stress, strain rate and temperature. The ideal or theoretical pressure required for extrusion of a fully dense material is expressed as

$$P = \sigma_0 \ln(r) \quad (3)$$

where σ_0 and r are yield stress and r is the extrusion ratio.

There are three varieties of powder extrusion process. These processes are mentioned below.

- (1) Loose powder is placed in the heated extrusion container and extruded directly through the die. This method has been developed for the extrusion of certain Mg alloy powder.
- (2) The powder is cold compacted and then hot pressed. The hot pressed compact is then extruded as per the conventional method. Al alloy powder billets are extruded by this method.
- (3) The metal powders are placed in a metallic capsule or can, heated and extruded with the can. A green metal powder compact may be canned or the powder may be cold pressed into a metal can under moderate pressure. The can is outgassed by evacuation at room or elevated temperature and sealed off before the can and powder are heated for extrusion (Upadhyay and Upadhyay, 2011).

Issa *et al.* (2017) fabricated amorphous nano SiO₂ reinforced Al MMC by powder metallurgy and hot extrusion method. They showed that addition of 1 wt% silica nanoparticle to aluminum matrix increased average hardness and tensile strength of the nano-composite by about 41.8% and 24.8%, respectively. They also observed that increasing nano-SiO₂ percentage decreased the tensile properties and ductility. Kim *et al.* (2019) fabricated tubular shape aluminum (Al) 6063/Al-3 vol% carbon nanotubes (CNT)/Al3003 functionally graded materials (FGMs) by hot extrusion process. They found that FGMs has high strength of 142 MPa and high elongation of 22%. Kurinskiya *et al.* (2015) studied hot extrusion of Be-Ti powder in copper and steel

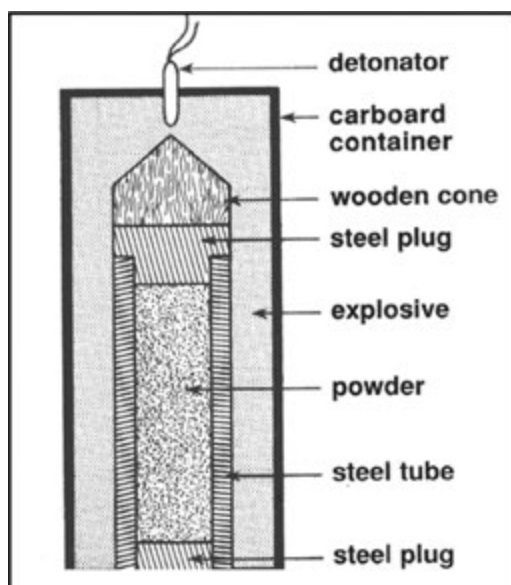


Fig. 14 A typical set up for the dynamic powder compaction. Reprinted with permission from German, R.M., 2005. Powder Metallurgy and Particulate Materials Processing. Princeton, NJ: Metal Powder Industries Federation, p. 332, Fig. 8.33. German, R.M., 1994. Powder Metallurgy Science, second ed. Princeton, NJ: Metal Powder Industrial Federation.

containers at 700 and 900°C, respectively. They observed that processing temperature has a great influence on the metal flow during the extrusion as well as formation of beryllide phases. Their study revealed that the brittle intermetallic phases were formed by processing at 900°C; while no evidence of reaction between beryllium and titanium was detected after extrusion at 700°C. [Jiao et al. \(2019\)](#) studied microstructure evolution and high-temperature tensile behavior of the 2.5 vol% TiBw/TA15 composites fabricated by powder extrusion.

Dynamic Powder Compaction

Dynamic powder compaction uses an accelerated mass which strikes the powder at very high velocity to supply the shock wave. The shock wave results in metallurgical bonding and sometimes fusion of the surface of particles. [Fig. 14](#) shows a typical set up for the dynamic powder compaction.

The process takes place in such a short time (microsecond or less) that there is no possibility for heat to be conducted away from the surface and thus localized melting or welding occurs. The liquid zone between the particles solidifies in the same time scale as its formation. The rapid cooling rate (10^6 – 10^8 °C s⁻¹) results in solidified material with extremely fine structure and imparts unique properties to the compact. This process allows non-equilibrium powder or powder mixture to be consolidated with either chemical reactions or degeneration of metallurgical structures.

[Mishra et al. \(2007\)](#) synthesized alumina-zirconium diboride in situ composite by novel SHS dynamic compaction process and studied the effect of addition of Ti as diluent in the reaction. They found that Vickers microhardness first increased with the addition of 5-wt% titanium and then decreased for further additions of titanium diluent up to 20 wt%. The maximum hardness was found as 2800 HV_{0.025}. [Mishra et al. \(2014\)](#) also fabricated alumina-titanium diboride in situ composite by self-propagating high-temperature synthesis (SHS) dynamic compaction and investigated the effect of compaction pressure on microstructure, toughness, hardness and modulus, oxidation behavior during synthesis. They achieved high hardness (average hardness: 22.684 GPa) with reasonable toughness (7.52 MPa m^{1/2}) and oxidation resistance up to 900°C temperature in Al₂O₃-TiB₂ composite. [Vorozhtsov et al. \(2017\)](#) investigated structural and mechanical properties of aluminum-based composites (Al-nanodiamonds and Al-Al₂O₃) processed by dynamic shock-wave compaction processing. They observed an increase in the hardness, compressive strength and elastic modulus of the composites after explosive compaction with the introduction of nanoparticles into the powder mixture. [Atrian et al. \(2015\)](#) investigated a comparative study on hot dynamic compaction and quasi-static hot pressing of Al7075/SiCnp (0, 5, and 10 vol% SiCnp) nanocomposite. They obtained higher compressive strength for quasi-static hot pressed samples than those produced under dynamic compaction. [Table 2](#) shows the summary of various composite fabrication methods using powder metallurgy. The main features of processing methods and density, grain structure of consolidated products of each method are shown.

[Table 3](#) shows a comparison of SiC-TiC composites fabricated by pressureless sintering, hot pressing (HP), hot isostatic pressing (HIP) and spark plasma sintering (SPS) ([Khodaei et al., 2018](#)). It has been observed from the table that pressureless sintering is not capable enough to produce composite with high densification (<98%) and improved mechanical properties. It is pressureless technique, hence some amount of residual pores are always present even sintering at comparatively higher temperature (2200°C). On the other hand, other pressure assisted sintering techniques (HP, HIP and SPS) are efficient enough to

Table 2 Summary of various composite fabrication methods using powder metallurgy

<i>Fabrication method</i>	<i>Main process features</i>	<i>Densification, grain structure of consolidated product</i>
Conventional sintering	Solid/liquid state sintering, Pressureless sintering, time required few hours	Low density level (max. around 90% of TD), High chance of grain coarsening, Cheap, simple process
Hot pressing/HIP	Uniaxial pressure/isostatic pressure, Time required few hours (1–2 h)	High level of density (Max. 98%–99% TD), Chance of grain coarsening, Expensive
Spark plasma sintering (SPS)	Consolidation by DC pulse, Time – few minute (5–10 min), Pressure assisted	99%–100% TD, Less grain coarsening, Nanostructure can be retained after sintering, Highly expensive.
Microwave sintering	Consolidation by microwave with suitable frequency (2.45 GHz)	Full densification, chance of grain coarsening
Powder forging	Consolidation by uniaxial stress (impact force)	Full densification, grains orientation along forging direction
Powder rolling	Consolidated by compressive force	Full densification, grains orientation along rolling direction
Powder extrusion	Consolidation by shear stress	Full densification, grains orientation along direction of extrusion
Dynamic powder compaction	Consolidation by shock wave within few minutes	Full densification, no chance of grain coarsening, rapidly solidified non-equilibrium structure

Note: The main features of processing methods and density, grain structure of consolidated products of each method are shown.

Table 3 A comparison of SiC–TiC composite fabricated by pressureless sintering, HP, HIP and SPS techniques

<i>Raw material</i>	<i>Second phase</i>	<i>Sintering method</i>	<i>Heat treatment temp. (°C)</i>	<i>Relative density (%)</i>	<i>Strength (MPa)</i>	<i>Fracture toughness (MPa m^{1/2})</i>	<i>Hardness (HV or GPa)</i>	<i>Ref.</i>
SiC, TiC, B, C	10 wt% TiC	Pressureless	2200	< 98	–	< 3	< 25	(Ohya <i>et al.</i> , 1992)
SiC, TiC, B, C	10 wt% TiC	HP	2200	98	< 550	< 4	–	(Ohya <i>et al.</i> , 1993)
SiC, TiC	25 wt% TiC	HIP	1850	> 99	682	3.97	2299 HV	(Shaoming <i>et al.</i> , 1996)
SiC, TiC	30 wt% TiC	SPS	1800	98	< 650	6.25	28	(Luo <i>et al.</i> , 2004)

Source: Khodaei, M., Yaghoobizadeh, O., Baharvandi, H.R., Dashti, A., 2018. Effects of different sintering methods on the properties of SiC–TiC, SiC–TiB₂ composites. *International Journal of Refractory Metals & Hard Materials* 70, 19–31.

produce composite with high densification (> 98%) and improved mechanical properties. Among three pressure assisted sintering techniques (HP, HIP, SPS), SPS require lowest temperature to produce composite with equivalent densification and mechanical properties. SPS is a unique consolidation technique, where activation of powder particles, spark effect, clean grain boundaries and minimal grain growth results in highest densification and mechanical properties even at lowest sintering temperature.

Conclusions

The article discusses about importance, relevance and uniqueness of powder metallurgy process as compared to other fabrication processes. The basic steps of powder metallurgy like powder fabrication, mixing/blending of powder, powder compaction and sintering are highlighted in brief. The basic principles of various composite fabrication techniques like pressureless conventional sintering and pressure assisted full densification processes are presented. The recent researches on fabrication of composites using various powder metallurgy processes are also summarized. Finally, a summary has been made on main features of various processing methods and consolidated product. It has been seen that pressureless conventional sintering is simple, economical process which consumes more time and less densification is achieved as compared to other pressure assisted sintering. On the other hand, uniaxial hot pressing/HIP and microwave sintering are complex processes, takes less time and higher density can be achieved than conventional sintering. SPS is best suited for consolidation of nanoparticle/ultrafine particle, where nanostructure can be retained after consolidation with full density, since it takes very less time (5–10 min). Powder metal working processes like powder rolling, powder extrusion and powder forging involves application of stress at higher temperature where metals are ductile. In all three techniques, full density can be achieved where grain orientation changes with deformation direction. In dynamic powder compaction, consolidation takes place by shock wave, generated by chemical reaction of explosive (SHS), takes very less time. Here, rapidly solidified non-equilibrium structure is generated after consolidation.

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Production of Metal Matrix Composites Via Additive Manufacturing

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Introduction

Compared to pure metals and alloys, metal matrix composites (MMCs) show a unique improvement in materials properties such as high specific strength, high specific stiffness, high wear resistance enabling their use in various applications such as turbine blades, brake disks, aerospace, cutting tools, and high temperature components (Rawal and Al, 2001; Russell and Lee, 2005; Chawla and Chawla, 2013). MMCs are composed of a ductile metal matrix, such as aluminum, copper, or titanium, combined with a secondary phased (usually a hard-ceramic reinforcement phase) in the form of filaments, fibers, or particulates. Improved mechanical performance (such as modulus, strength, and creep life, as well as reduced wear rates) can be achieved when a secondary hard phase is introduced into a ductile metal matrix to fabricate a composite system (Ibrahim *et al.*, 1991; Ramesh and Ahamed, 2011). Basically, the remarkable properties of MMCs are derived from the evolved microstructures that develop during processing.

Different methods can be used in MMCs production such as solid-state processing (e.g., powder blending and consolidation, diffusion bonding, and physical vapor deposition), liquid-state (e.g., stir casting, squeeze casting, infiltration process, spray deposition), and in-situ processing (by chemical reactions leading to reinforce phase formation) (Chandra Kandpal *et al.*, 2015; Almangour, 2018). Typically, liquid-state and vapor-state processing often lead to inhomogeneous dispersions of the second phase within the metal matrix. To achieve a more homogenous or more well defined reinforcement distribution is an on-going research area of importance. Traditional MMC manufacturing methods include (1) stir casting (Thomas *et al.*, 2014) and powder metallurgy (Ye *et al.*, 2008). However, either of these methods show limitations such as the possible reaction of the secondary phase with the melt or a tendency for settling during casting (Hashim *et al.*, 1999), while particle morphology and size are restrictive characteristics (e.g., spherical or angular particulates, flat sheets, prismatic sections) in injection molding (Gofrey *et al.*, 2000). Nevertheless, combination of metal with a reinforced powder is not easily obtainable because of a few issues such as weak interfacial reinforcement-matrix bonding, inhomogeneous dispersions of the second phase, residual stresses, crack formation at the interfaces, dislocations, thermal mismatches leading to work hardening between composing phases, and potential variations in metal matrix precipitation kinetics due to presence of reinforcements. Moreover, the formation of agglomerates of the reinforced phase needs to be prevented during solid-state and liquid-state processes. Typically, post-processing or machining to produce a final usable geometry is required which will add further to the part production costs.

Based on all these issues and demands, additive manufacturing can be considered as an alternative to overcome many limitations caused by traditional MMCs processing methods. Additive manufacturing, also known as three-dimensional (3D) printing, provides a processing route to fabricate complex, overhang structures mostly from powdered materials. AM technology introduces a set of new manufacturing methods, processes and technologies that produce parts through material addition, in contrast to the established traditional subtractive manufacturing methods. Design and printing of complex geometries, possibility of light weight component printing, gradient structures, waste elimination and recycling of the used materials are merits of AM technology (Giannatsis and Dedoussis, 2009; Mostafaei *et al.*, 2018). Rapid prototyping is the broadest use of AM principles, by designing of models and prototypes for concept assessment as well as functional testing of new products. While AM processes are becoming considerably important in manufacturing of novel materials, majority of the current efforts are focusing on process parameter optimization of well-matured alloys and compounds from powdered materials to attain reproducible microstructure and properties, comparable to or better than that of the conventionally processed parts; however, there are limited studies on the AM of MMCs. Here, a comprehensive literature review is conducted to demonstrate the most recent developments to fabricate MMCs parts using the various AM processes. AM methods are compared together in terms of the quality, achievements, and challenges.

Additive Manufacturing Processes for Fabrication of MMCs

Powder-based additive manufacturing is versatile to process different powdered materials for composite production. Generally, there are two main categories to fabricate composites including “ex-situ” and “in-situ” reinforced MMCs. In the ex-situ approach, composition of the starting powdered materials remains in the manufactured composite. In fact, the reinforcement is externally synthesized, then is pre-mixed with the matrix powdered materials (sintering of the powder particles is needed) or fed separately the melt pool during fusion-based AM process. In contrast, chemical reactions occur during in-situ approach leading to the production of reinforcement particles within the matrix. In other words, the reinforcement is synthesized in the matrix through the chemical reactions which is occurred during AM process. Different AM processes can be applied for MMCs production such as powder bed fusion (PBF), direct energy deposition (DED), binder-jet 3D-printing (BJ3DP) and hybrid 3D-printing. A schematic of

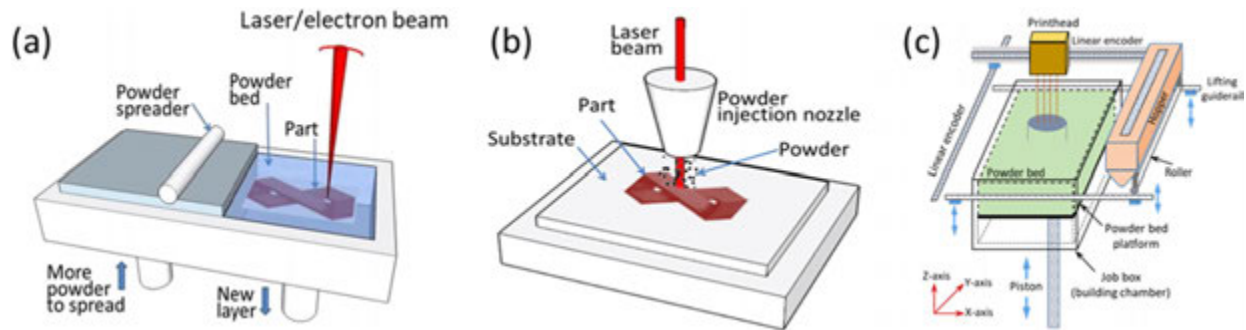


Fig. 1 Schematic of (a) powder bed fusion, (b) direct energy deposition, and (c) binder jet 3D printing. Reproduced from DebRoy, T., Wei, H.L., Zuback, J.S., *et al.*, 2018. Additive manufacturing of metallic components – Process, structure and properties. *Prog. Mater. Sci.* 92, 112–224. Mostafaei, A., De Vecchis, P.R., Buckenmeyer, M.J., *et al.*, 2019. Microstructural evolution and resulting properties of differently sintered and heat-treated binder jet 3D printed stellite 6. *Mater. Sci. Eng. C* 102, 276–288.

these AM processes is illustrated in Fig. 1. In the following, each of these processes are explained in detail and relevant examples are presented.

Fusion-Based AM Processes

Different powder based fusion AM processes such as selective laser melting/sintering (SLM/SLS), direct metal laser sintering (DMLS), electron beam melting (EBM), and direct energy deposition (DED) can be used to fabricate MMCs. In the laser based PBF (L-PBF) or electron beam PBF (E-PBF) processes, a layer of powdered materials is spread on a bed, then a focused laser or electron beam is directed to the area of interest to join powders. In the SLS and DMLS processes where sintering (partial melting) of powder particles occur, pre-mixed powders are used, leading to the production of ex-situ reinforced MMCs. In contrast, full-melting of powdered materials is achieved in SLM and EBM, thus, they can be used for fabricating in-situ reinforced MMCs through activating chemical reactions between the constituents existing in the system.

PBF begins with a CAD model and the part should be oriented on the build plate. Sometimes, support structure is added for complex, overhang structures to prevent distortion during printing. Then, the following steps are defined prior to running the AM machine; the slicing of the CAD model into planar layers (defined by layer thickness), and defining print processing parameters such as a scan pattern, laser power, scan speed, and hatch spacing. L-PBF operates within an inert chamber and the powder is processed by a raster motion of the laser beam, resulting in melting and rapid solidification of overlapping melt tracks. There are a few differences between E-PBF and L-PBF. Firstly, electron beam melting works under the vacuum condition. Further, the E-PBF process relies on a two-step sequence including (1) pre-heating of the powder bed known as pre-sintering each layer of powder to prevent electro-static charging and repulsion of the powder particles and (2) fusing of powder particles by an additional pass of electron beam. The pre-heat condition allows a fast scanning speed of the electron beam. While pre-heating is not required in L-PBF, it is also most commonly used in order to increase process speed and control. PBF facilities typically operate within the ranges of power of 50–1000 W, scan speed of 10–1000 mm/s and dimensional accuracy of 40–200 μm (DebRoy *et al.*, 2018).

In powder-based direct energy deposition (DED), powder particles are fed into the print spot through a nozzle and the melt path and molten pool are created by a laser or electron beam. There are various DED processes including direct laser deposition (DLD), laser metal deposition (LMD), laser engineered net shaping (LENS), laser consolidation (LC), and laser cladding. The deposition process begins with a CAD model and printing occurs layer-by-layer on a substrate part or build plate. To protect the molten materials from oxidation and provide a better powder flow into the molten pool, a shielding gas such as argon is used. To prevent distortion during fabrication of complex geometry with overhang features, an appropriate support structure is required. The print processing conditions such as the scan speed of the laser source and feed rate of the feedstock powder are either pre-set or controlled in-process by appropriate sensors. DED processes are capable of fabricating both ex-situ and in-situ reinforced MMCs. While surface finishing is often required for all metal AM processes, compared to the PBF process, the quality of the surface finish is low in DED and parts need further finishing operations to attain the desired surface quality. The DED process typically operates within the ranges of 100–3000 W, scan speed of 50–20 mm/s and dimensional accuracy of 500–1000 μm (DebRoy *et al.*, 2018).

The ceramic reinforcing particles can be produced separately and added to the matrix which is called ex-situ reinforced MMCs. One of the main advantages of the powder bed fusion AM processes is the capability of incorporating reinforcements either ex-situ or in-situ into the metal matrix structure. In ex-situ reinforced MMCs, the size and shape of ceramic reinforcements are defined by the premixed powder conditions, whereas, the in-situ reinforced MMCs the desired reinforcing particles synthesized from the chemical reactions. Different reinforced particles have been used in PBF AM processes to fabricate MMCs parts such as TiC (Gu *et al.*, 2015; Yuan *et al.*, 2015; Gård *et al.*, 2006; AlMangour *et al.*, 2016; Gu *et al.*, 2012; Sano and Srivatsan, 2016), Al_2O_3 (Han *et al.*, 2016), TiB_2 (Zhang *et al.*, 2016; Shishkovsky *et al.*, 2017), carbon (Zhao *et al.*, 2016; Wang *et al.*, 2016), and SiC (Song *et al.*, 2013; Ghosh

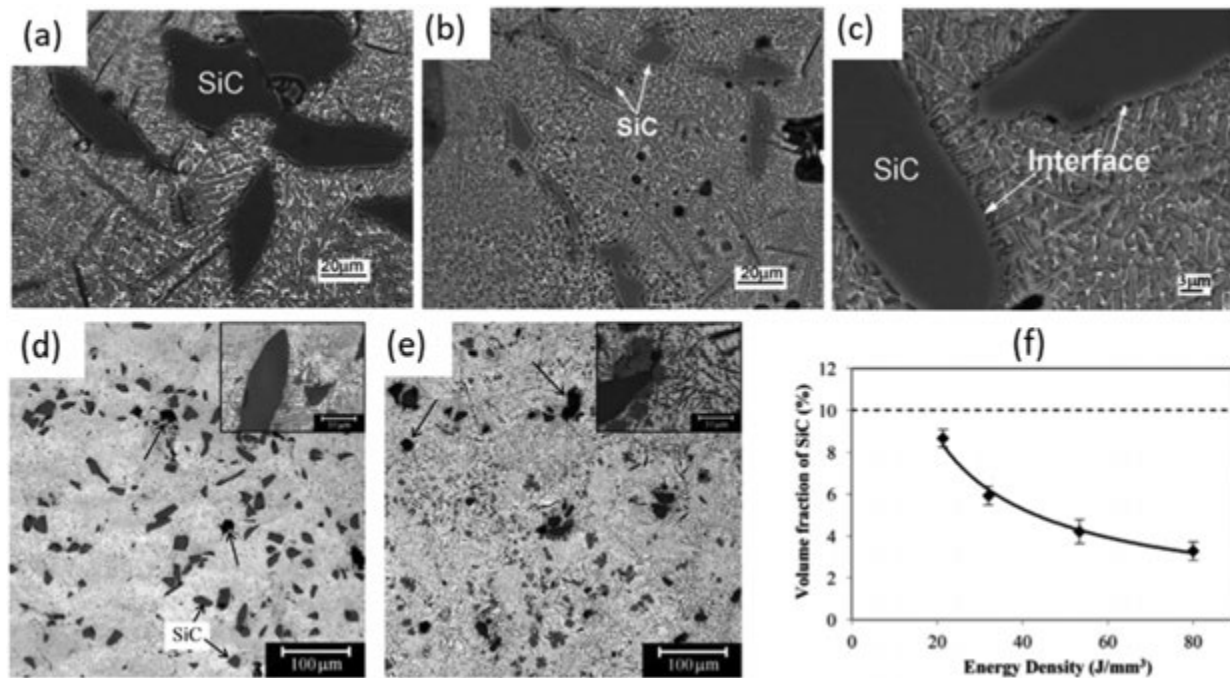


Fig. 2 SEM micrographs from LPBF processed Al-4.5Cu-3Mg matrix mixed with (a) coarse and (b) fine SiC powder. (c) Interface of SiC particles and Al matrix in which cracking may initiate and propagate. Optical micrographs of the SiC reinforced MMCs fabricated with laser energies of (d) 21 J/mm², (e) 71 J/mm², and (f) variation in volume fraction of SiC as a function of energy density during LPBF process. A decrease in the amount of SiC particles (angular dark gray phase) was seen at the higher energy density. Reproduced from Ghosh, S.K., Saha, P., Kishore, S., 2010. Influence of size and volume fraction of SiC particulates on properties of ex situ reinforced Al-4.5Cu-3Mg metal matrix composite prepared by direct metal laser sintering process. *Mater. Sci. Eng. A*. 527, 4694–4701. Astfalck, L.C., Kelly, G.K., Li, X., Sercombe, T.B., 2017. On the breakdown of SiC during the selective laser melting of aluminum matrix composites. *Adv. Eng. Mater.* 19, 1–6.

et al., 2010; Astfalck *et al.*, 2017). During the PBF process, one needs to consider potential dissolution of the reinforcement in the melt pool and formation of a few in-situ phases. Moreover, two other drawbacks related to the ex-situ reinforced MMCs are the weak interfacial bonding between the ceramic reinforcing particles and the metal matrix as well as the poor wettability at the interface between the particles and matrix.

Aluminum-based MMCs

As an example for the ex-situ MMC, SiC reinforcement particles were added to Al matrix and parts were fabricated using LPBF (see Fig. 2). Fabrication of MMCs composite from aluminum matrix is challenging due to low wettability between the reinforcing particles and the Al matrix, low laser energy absorption by aluminum and high propensity of aluminum to react with oxygen at high temperatures. Ghosh *et al.* (2010) and Ghosh and Saha (2011) processed SiC reinforced Al-4.5Cu-3Mg composite using LPBF with varied size and volume fraction of the SiC reinforcement. It was seen when SiC particle size decreased, density of the final product decreased due to potential agglomeration of powder particles leading to improper flowability and melting during LPBF process. In contrast, when the volume fraction of SiC particles increased from 10% to 30%, density increased from 2.3 g/cm³ to 2.5 g/cm³. Microhardness results showed higher hardness with a higher fraction of SiC or with finer particles. Additionally, Astfalck *et al.* (2017) showed that higher laser energy could affect dissolution of SiC particle in the matrix (Astfalck *et al.*, 2017). It was found that the SiC reinforcement particles were partially melt and dissolved in the Al matrix and led to the formation of a few in-situ phases. Coarse un-melted SiC particles remain in the matrix to form ex-situ MMCs. When SiC particle dissolve in Al matrix, C may react with Al and forms needle-like Al₄C₃ and Si (see Fig. 2(e)).

Typically, the type and ratio of starting powders as well as the processing parameters during fusion-based AM processes influence the heat input and the duration of reaction in melt pool. Compared to ex-situ reinforced MMCs, in-situ synthesized ceramic reinforced particles have attracted attention due to the following reasons:

- (1) addition of the second phase reinforcement particles in mixed powders could increase porosity of the LPBF process part;
- (2) potential for control over size of the reinforcement particles with improved distribution;
- (3) higher thermodynamic stability of the in-situ synthesized reinforcement ceramic particles for high temperature application;
- (4) better wettability of the reinforcement particle with metal matrix due to un-oxidized and contaminant-free surfaces of the in-situ synthesized reinforcements.

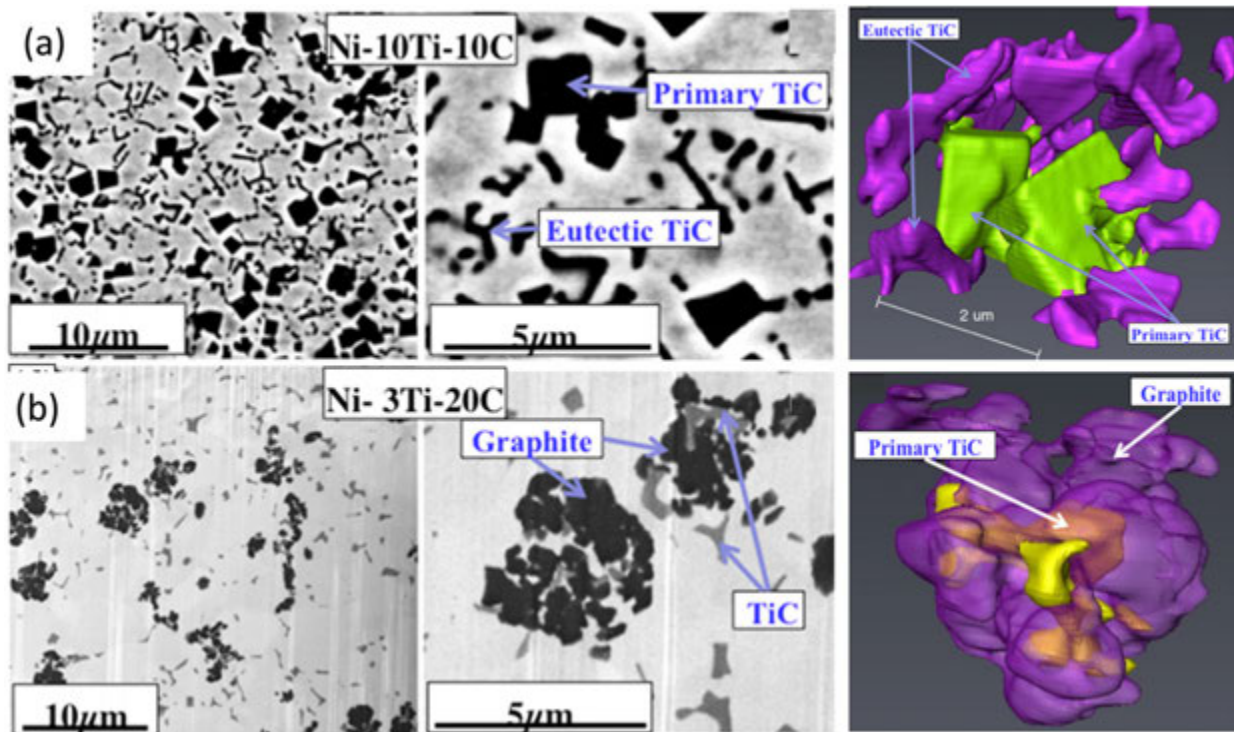


Fig. 3 SEM micrographs and 3D reconstructed images of DED processed Ni-TiC MMC composites: (a) Ni-10Ti-10C and (b) Ni-3Ti-20C. Reproduced from Borkar, T., Gopagoni, S., Banerjee, R., Hwang, J., Tiley, J., 2014. Laser-deposited in situ TiC-reinforced nickel matrix composites: 3D microstructure and tribological properties. JOM. 66, 935–942.

Nickel-based MMCs

Nickel superalloys have been widely used in aerospace, petrochemical and nuclear energy, and high temperature applications due to their outstanding properties such as mechanical strength and fatigue life, low thermal expansion and high corrosion resistance. TiC with a very high hardness and melting point is very brittle, however, it can be used as a reinforcement in nickel alloys to further improve properties. DED was applied to uniformly disperse TiC reinforced particles formed during in-situ reaction of C/Ti (Sano and Srivatsan, 2016; Borkar *et al.*, 2014). Based on the C/Ti ratio, primary (cuboidal shaped), and eutectic (plate-shaped) TiC reinforcements were formed. As shown in Fig. 3, when the Ti/C ratio is 1, both fine needle like eutectic and cuboidal primary TiC precipitates formed. When the ratio is higher (e.g., ~7), black graphite phase along with dark gray TiC precipitates were detected. Hardness measurements showed that the former microstructure had higher hardness (370 HV) and friction coincident.

Non-Beam-Based AM Processes

Compared to PBF and DED processes in which a heating source melts powder particles, binder jetting is a non-beam-based AM process. This method is a powder bed technique in which a layer of powder is spread on the surface using a roller and a printhead sprays binder onto surface to fabricate parts based on a CAD model. This process repeats multiple times to finish the printing step. The main print processing parameters during binder jetting include powder layer thickness, binder saturation, print speed and drying time. Binder jetting is a solid-state processing, in which pre-mixed powder particles are 3D-printed followed by post-processing including curing (to increase green part strength) and densifications (such as infiltration and sintering). Curing depends on binder composition but it usually occurs at 180°C–200°C for up to 8 h. Infiltration is a route of densification using an alloy with a lower melting temperature compared to the 3D printing matrix (such as bronze with steel) to eliminate residual porosity and achieve full density with negligible dimensional changes. The other densification method for binder jetted parts is sintering where powder particles are locally melted. During sintering, temperature, holding time, and atmosphere play an important role in the final resulting microstructure and properties (Mostafaei, 2018).

Unlike part production from pure metals and alloys, 3D printing of metal matrix composites (MMCs) is not that common. MMCs are material systems with two constituents: one is a harder reinforcement material (the skeleton) and the other is a metal that surrounds the reinforcement. The harder material can be a metal or a ceramic phase. In terms of binder jet 3D printing, these materials can be processed two ways: (1) by printing the composite powder mix and finishing with a sintering post-processing step or (2) by printing the reinforcement material and finishing with a melt infiltration step of the metal matrix material.

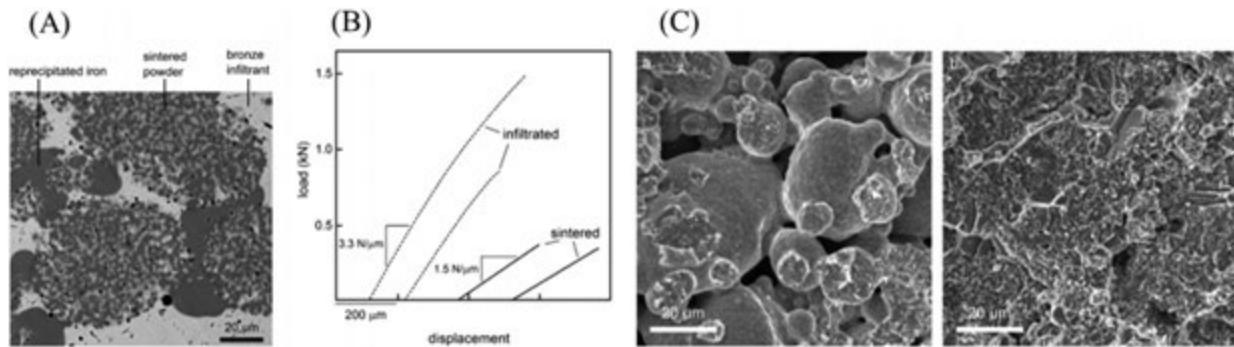


Fig. 4 (a) SEM micrograph of the infiltrated iron-based material with bronze, (b) load-displacement curves from bend tests, and (c) SEM micrographs of (left) a sintered and (right) an infiltrated bend test specimen's fracture surface. Reproduced from Cordero, Z.C., Siddel, D.H., Peter, W.H., Elliott, A.M., 2017. Strengthening of ferrous binder jet 3D printed components through bronze infiltration. *Addit. Manuf.* 15, 87–92.

Stainless steel-based MMCs

Steel and bronze are common matrix and reinforcement materials used for MMC production with the binder jet 3D printing process. This is because the wetting is sufficient and there is limited solubility of one material into the other. [Cordero et al. \(2017\)](#) binder jetted iron followed by bronze infiltration to increase strength of the MMC by filling the voids and lessening stress concentrators at particle necks compared to sintering the same part (see [Fig. 2](#)). Different phases were seen such as sintered iron powder, bronze infiltrant, and reprecipitated iron. Mechanical behavior of the fabricated part (load-displacement from bend tests) showed that the infiltrated part had an average transverse rupture strength of 570 MPa, over four times higher than that of the sintered specimens. Fractography study showed that brittle fracture at the interparticle necks occurred in the sintered part; however, the infiltrated one failed primarily by transparticle crack propagation.

In other studies ([Do et al., 2017](#); [Do et al., 2015](#)), small amount of boron compounds were added to the composition as a sintering additive element to enhance densification. In fact, sintering additives such as boron compounds can facilitate sintering due to liquid phase formation ([Huang et al., 2019](#)). [Do et al. \(2018\)](#) binder jetted stainless steel 316 L incorporated with different amount of sintering additives (0–0.75 wt%) such as B, BC, and BN into the starting powder mix between, the final relative density of $\sim 99.7\%$ was achieved after sintering in a vacuum atmosphere at 1350°C . As expected, the sintering additives improved densification behavior and led to a smooth surface finish (see [Fig. 3](#)).

Titanium-based MMCs

Titanium is a light metal and it has been used as dense and porous compounds in aerospace, automotive, and biomedical fields due to their high strength-to-weight ratio, superior corrosion resistance and excellent biocompatibility. To develop the concept of MMCs fabrication, [Sheydaei and Toyserkani \(2018\)](#) 3D-printed Ti-TiB periodic composites via binder jetting the Ti matrix reinforced periodically by the extrusion of a custom-developed highly loaded resin containing titanium di-boride (TiB_2) particles followed by a low-temperature pressureless sintering. [Fig. 4](#) shows the fabricated parts and the microstructure of sintered samples. Two main variables including the ceramic volume fraction and sintering protocol were evaluated and properties such as density and mechanical strength were analyzed. Based on the sintering temperature and designing features of the printed parts, porosity ranging from $28 \pm 1.4\%$ to $38 \pm 2.0\%$ was attained from the Archimedes method. As expected in binder jetted parts, higher dimensional deviation and higher shrinkage was seen in the height (z-direction) of parts compared to x- and y-directions. Additionally, the volume fraction of TiB affected microstructure of the formed of the TiB_2 and the resultant physical properties and mechanical properties. As the sintering temperature increased from 1200°C to 1400°C , TiB_2 had a chance to grow further and form needle-shape reinforced particles. Mechanical properties ranging from 1.6 ± 0.2 GPa– 3.7 ± 0.4 GPa for the Young's modulus and 83.9 ± 18.7 MPa– 165 ± 13.2 MPa for the yield strength were obtained. The stiffness values increased remarkably as the sintering increased to 1400°C . In another work, porous TiC/Ti₆Al-4V MMC parts were produced by novel hybrid 3D-printing/sintering method using a blend of Ti-6Al-4V and dextrin powders as a precursor material ([Yadav et al., 2019](#)). After binder burnout at 700°C for 1 h in Ar atmosphere, there was 26 wt% carbon residue in the 3D-printed part that could potentially be a source for TiC formation in agreement with in-situ MMCs production using nickel superalloys ([Enrique et al., 2018](#)). When layer thickness increased from 150 μm to 175 μm , green part density as well as sintered density decreased. In addition, pore size after sintering (regardless of temperature) was higher for 175 μm layer thickness. The highest density of 5.25 g/cm^3 was obtained for parts sintered at 1500°C for 8 h with a layer thickness of 150 μm , in which maximum values of Young's modulus, compressive strength, bending strength and hardness were found to be 51 GPa, 701 MPa, 285 MPa, and 1.8 GPa, respectively.

Tungsten-based CMMs

Tungsten (W) is a good composite reinforcement candidate because it is difficult to process in pure amounts. Tungsten can be processed with metals of lower melting temperatures with liquid-phase sintering, and it can also remain mostly undissolved

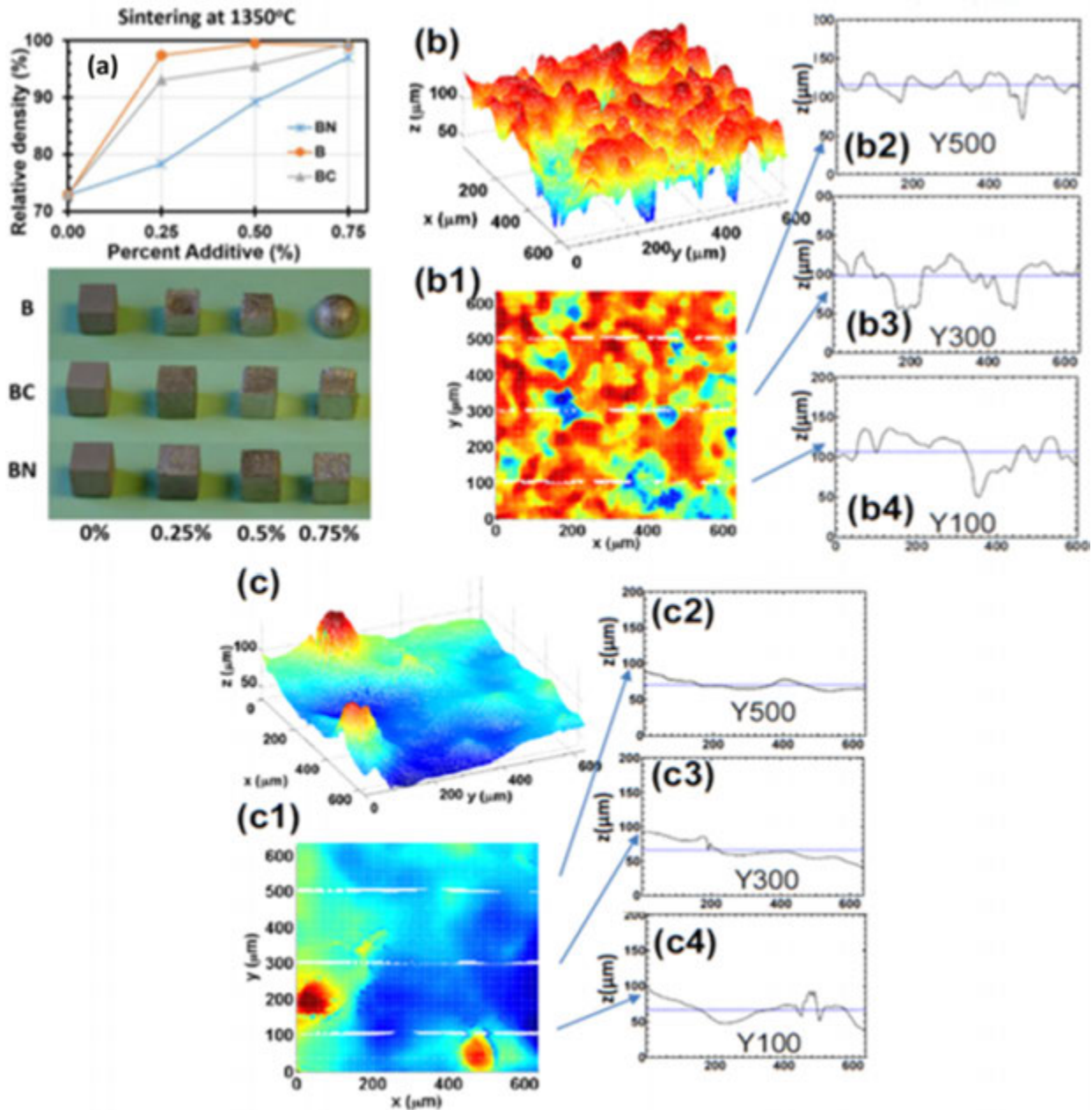


Fig. 5 (a) Picture and relative density results of mixed SS 316 L boron compounds sintered in vacuum atmosphere, (b) surface topologies of binder jetted parts after sintering at 1300°C, and (c) surface topology of mixed powder with 0.5% boron. Reproduced from Do, T., Bauder, T.J., Suen, H., *et al.*, 2018. Additively manufactured full-density stainless steel 316 L with binder jet printing. Proceedings of the ASME 2018 13th International Manufacturing Science and Engineering Conference MSEC2018, 1–10.

while providing good wetting with most other metals to create composites with pressureless melt infiltration. Pure W powdered material was used to binder jet complex part followed by sintering at 1385°C for 2 h with the achieved maximum density of 99.7% with shrinkage of ~19%, tensile strength of 770 MPa and elongation of 8.6% (Stawovy *et al.*, 2019). Lipke *et al.* (2010) binder jetted ZrC/W-based composites with a relative density of ~57% (see Fig. 2). To increase the green part strength for preform handling, part was partially sintered at 1400°C for 2 h to let neck formation between WC particles. Then, the porous rigid preforms were exposed to molten Zr_2Cu at 1150°C–1300°C and ambient pressure. Zr in the melt reacted with WC forming ZrC and W products in which the prior pores were filled by ZrC and the maximum relative density of 94% was attained. The produced ZrC/W-based MMCs could retain the original shape and dimensions with up to 1% shrinkage compared to the WC preforms. The infiltrated 3D-printed part showed a layered morphology (with alternating ZrC-rich and W-rich layers) whereas dense composites formed from the infiltrated pressed part indicated a relatively uniform distribution of ZrC and W phases. (Figs. 6–8).

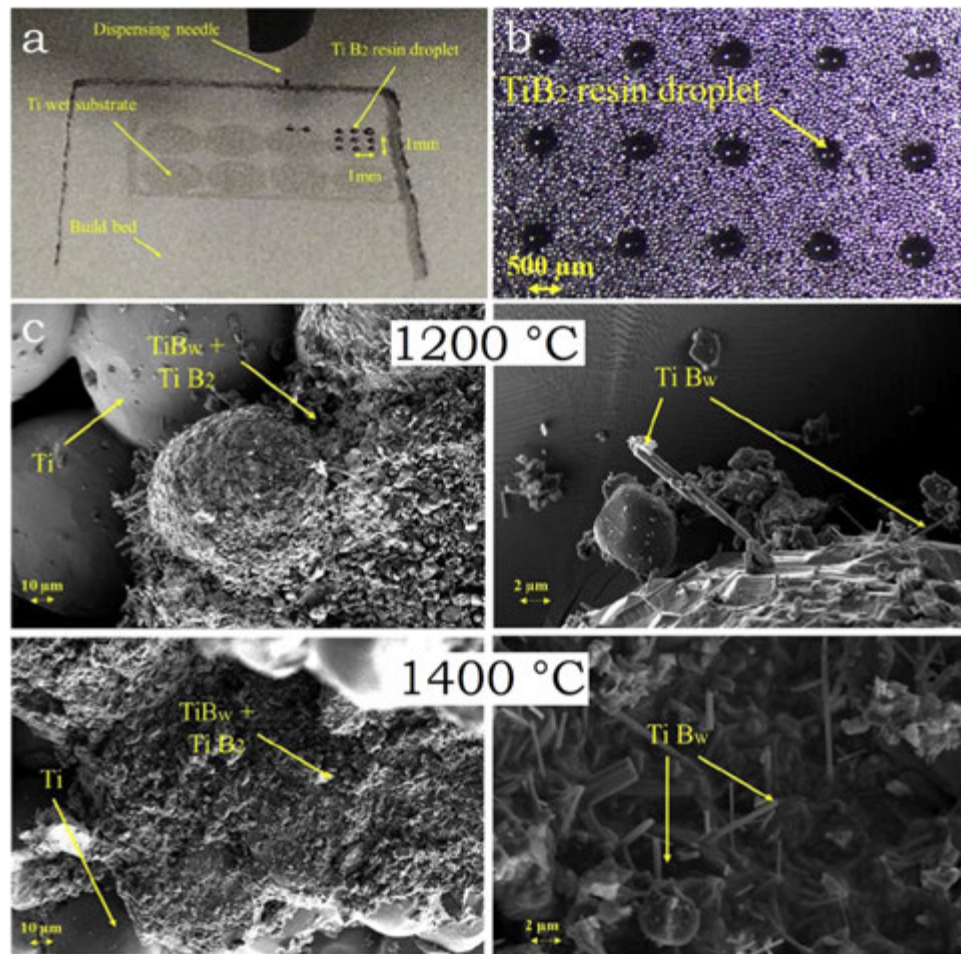


Fig. 6 (a) A sample of 3D-printing one layer of composite. (b) Test sample illustrating the ceramic resin pattern after polymerization on Ti substrate, and (c) SEM micrographs of Ti-TiB₂ reaction zone as a function of sintering temperature. Reproduced from Sheydaei, E., Toyserkani, E., 2018. A new approach for fabrication of titanium-titanium boride periodic composite via additive manufacturing and pressure-less sintering. *Compos. Part B Eng* 138, 140–148.

Tungsten carbide-based CMMs

WC-Co is widely used in various industries due to its high strength, hardness, and stiffness at high temperatures, particularly in metal working, mining industries, and wear coating applications (Yuan *et al.*, 2013). Typically, WC-Co is composed of WC particles and Co matrix material and due to a significant difference of melting points between these two materials, liquid-phase sintering through cobalt and eutectic melt is the main mechanism for densification. Kumar (2018) conducted selective laser sintering of WC-Co powder in which parts with various size and thickness were fabricated. Parts with different size and wall thickness were produced with Young's modulus and yield strength of 508 GPa and >2000 MPa, respectively. However, two issues were seen in the SLS produced parts including micro-crack formation and heterogenous microstructure. Enneti *et al.* (2018) and Enneti and Prough (2018) introduced binder jetting to produce parts from WC-Co composite powder. Sintering under pressure at 1485°C for 5 min led to higher density as well as uniform distribution of WC grains in Co matrix; however, the etched microstructure shown in Fig. 5(a) revealed grain coarsening uniformly distributed in the microstructure and those clusters were present at ~10 vol%. Further testing was conducted using optimum sintering conditions including hardness ($1287 \pm 45 \text{ HV}_{30}$) and fracture toughness ($17 \pm 1 \text{ MPa m}^{1/2}$), in agreement with the reported properties of conventionally produced medium grain size WC-12%Co. Cramer *et al.* (2019c,b) studied 3D-printing of WC preforms infiltrated by cobalt (see Fig. 5(b)). Results showed that pre-sintered part followed by Co infiltration resulted in a uniform microstructure in which WC grains were properly wetted by Co matrix and the maximum relative density of 98.5% with ~15% shrinkage was attained. However, WC grain growth was reported that could affect mechanical properties. Since infiltration of preform WC may lead to the formation of large pits and missing parts of the 3D printed WC, Cramer *et al.* (2019a) proposed using the WC-20 wt% eutectic composition where the distortion and shrinkage were minimized.

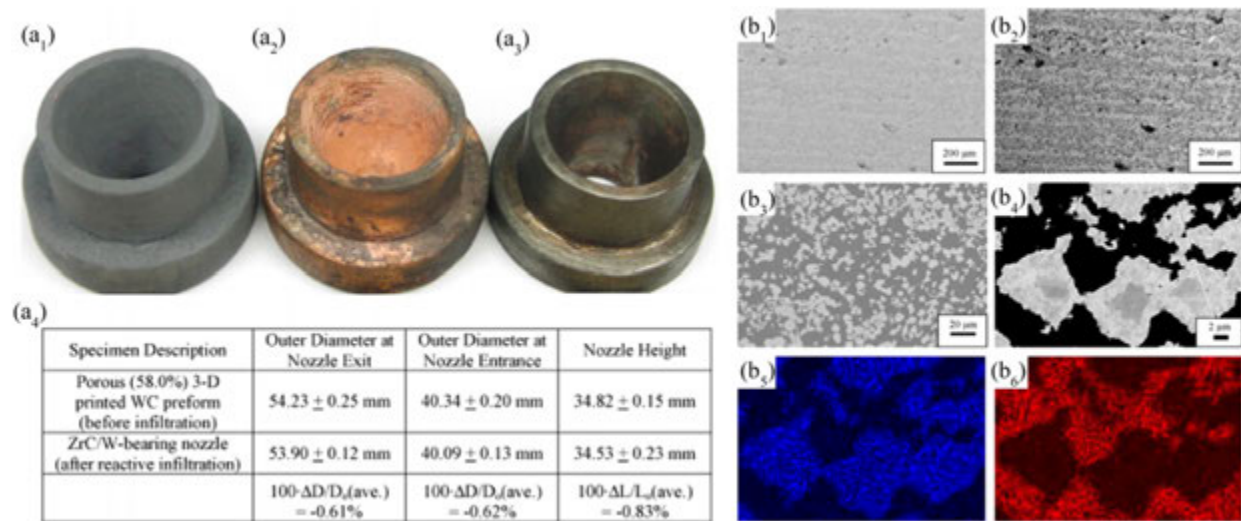


Fig. 7 Optical micrographs of rocket nozzle-shaped samples at various stages of fabrication via 3D printed parting from WC powder and infiltration. (a₁) A porous, rigid WC preform was prepared followed by binder burnout and partial sintering for necking of WC particles, (a₂) infiltrated parts with Zr₂Cu melted at 1150°C for 30 min, then further reaction above the melt at 1300°C for 2 h, (a₃) final product after surface cleaning, (a₄) dimension measurement results, and (b_{1–4}) SEM micrographs with corresponding EDS elemental mapping of (b₅) W and (b₆) Zr. Reproduced from Lipke, D.W., Zhang, Y., Liu, Y., Church, B.C., Sandhage, K.H., 2010. Near net-shape/net-dimension ZrC/W-based composites with complex geometries via rapid prototyping and Displacive Compensation of Porosity. *J. Eur. Ceram. Soc.* 30, 2265–2277.

Challenges and Opportunities of MMCs Fabrication Using AM Processes

Similar to any processing method, MMCs fabrication with AM processes may have a few challenges. In the following, the most common concerns using AM processes are addressed (Gård et al., 2006; Ghosh et al., 2010; Ghosh and Saha, 2011; Hegab, 2016; Quan et al., 2015; Yakout et al., 2017):

- (1) The determination of AM process (fusion-based or non-beam-based AM technique) as well as optimum process parameters for each powdered material.
- (2) The thermal history and residual stress during fusion-based AM process during the deposition of subsequent layers resulting in microstructure variations in each layer and possible micro-crack formation. The thermal gradient and residual stresses might be induced in the inter-track or inter-layer areas which have detrimental effect on mechanical properties.
- (3) Different defects may form in the 3D-printed parts depending on the printing method and processing parameters. For example, binder jetted green parts can have ~50% porosity which needs to be removed by post processing. In PBF and DED, common defects are keyhole and lack of fusion porosities as well as balling effect which are related to the combination of laser power, scan strategy and scan speed. These issues will affect surface finish and part integrity influencing properties.
- (4) Unwanted chemical reactions between pre-mixed powder will change the designed composition and microstructure of the final MMCs. This is challenging in ex-situ reinforced MMCs while the chemical reactions between the powder particles are essential to develop in-situ reinforced MMCs.
- (5) Since the reinforced compounds are usually hard materials such as ceramics, micro-cracking may form at the reinforcement/matrix interface which is mostly associated with the substantial difference in physical and mechanical properties of reinforcements and the matrix. These micro-cracks may influence the functionality and performance of 3D-printed parts and cause failure.
- (6) Some issues occur during AM processes such as dissolution of alloying element(s), loss of specific materials and micro-segregation of the reinforcing materials.

In order to overcome these challenges, the following suggestions are proposed (Scott et al., 2012; Gao et al., 2015; Hanzl et al., 2015; Górski et al., 2013; Bourell et al., 2009; Hrabec and Quinn, 2013; Guo and Leu, 2013):

- (1) Topology optimization and new designs for AM of MMCs.
- (2) Process parameter optimization based on the applied AM process for any MMCs. A dataset for various MMCs is needed to understand the effect of print processing parameters on resulting microstructures. This is needed in order to achieve defect-free part production with surface integrity, desired microstructure and mechanical properties of the 3D-printed parts.
- (3) Creating a real-time process control (e.g., using machine vision or other sensors) for the AM systems.
- (4) Developing/modifying AM machines (possibly hybrid AM process to produce multi materials) to fabricate new MMCs (in-situ or ex-situ mechanisms).

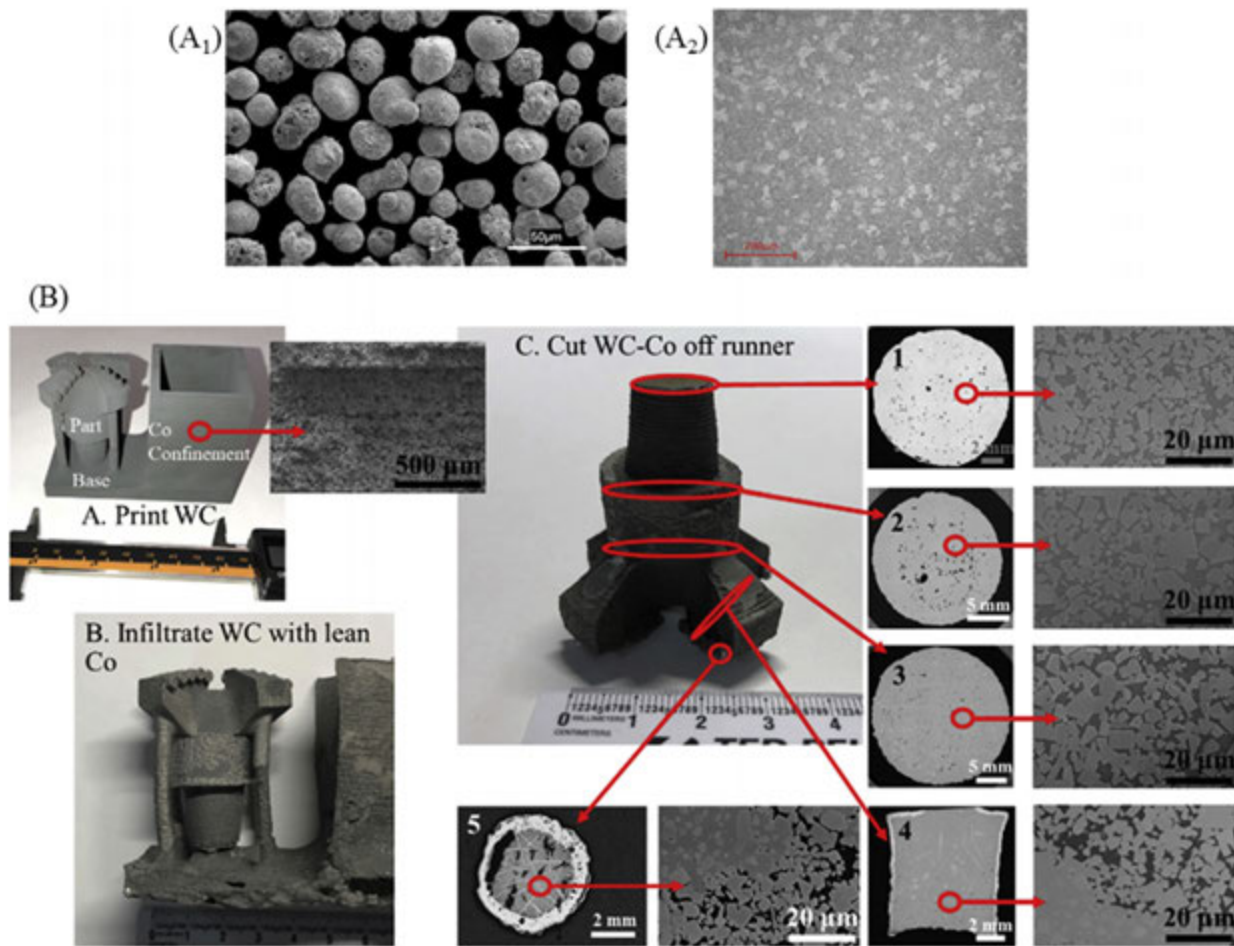


Fig. 8 (A₁) SEM micrograph showing morphology of the used WC-12%Co powder, and (A₂) Etched microstructure of a sample pressure sintered at 1485°C. (B) Set up, sequence, and microstructural results of infiltration of WC with Co. Reproduced from Enneti, R.K., Prough, K.C., Wolfe, T.A., *et al.*, 2018. Sintering of WC-12%Co processed by binder jet 3D printing (BJ3DP) technology. *Int. J. Refract. Met. Hard Mater.* 71, 28–35. Enneti, R.K., Prough, K.C., 2018. Wear properties of sintered WC-12%Co processed via binder jet 3D printing (BJ3DP). *Int. J. Refract. Met. Hard Mater.* 78, 228–232. Cramer, C.L., Wieber, N.R., Aguirre, T.G., Lowden, R.A., Elliott, A.M., 2019c. Shape retention and infiltration height in complex WC-Co parts made via binder jet of WC with subsequent Co melt infiltration. *Addit. Manuf.* 29, 100828.

Conclusion

Additive manufacturing processes provide versatile fabrication methods for the production of MMCs. Based on the metal matrix and reinforcement phase, one may choose a fusion-based (e.g., laser powder bed fusion, electron beam melting and direct energy deposition) or non-beam-based (e.g., binder jetting) process to fabricate in-situ or ex-situ composites. Since both in-situ and ex-situ MMC productions are available for different AM processes, it is necessary to know the advantages and drawbacks for each AM process choice prior manufacturing of MMCs via AM. New machines designs and material options will be developed in the coming years which will rapidly drive forward this exciting technology to be used in a wider range of application areas.

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Matrix and Reinforcement Materials for Metal Matrix Composites

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Introduction

Modern engineering composite materials can be said to have “engineered mechanical properties” in that the distributed components/reinforcements tends to have nano-meter to micro-meter sizes (Moghadam *et al.*, 2015). Under all service conditions, the conventional alloys do not always provide the necessary characteristics and it can be overcome by reinforcing those alloys with ceramic particles (Bhoi *et al.*, 2019; Rashad *et al.*, 2015; Ramnath *et al.*, 2014; Bodunrin *et al.*, 2015). Reinforced metal matrix composites of this kind are widely known as MMCs. MMCs have gained significant attention in the aerospace, aircraft, and automotive industries due to their elevated strength, stiffness, Young's modulus, fatigue strength, corrosion resistance, wear resistance, and low density compared to unreinforced alloys (Shirvanimoghaddam *et al.*, 2017; Baradeswaran and Perumal, 2014; Liu *et al.*, 2013; Sharma *et al.*, 2015). Ceramic particles like SiC, B₄C and Al₂O₃ are readily accessible and have been used since the introduction of MMCs and are also inexpensive. The advancement of manufacturing technologies has also enabled MMCs to be reinforced with several types of prospective ceramic particles such as SiO₂, SiC, TiO₂, Al₂O₃, TiC, B₄C, etc. (Knowles *et al.*, 2014; Boostani *et al.*, 2015; Toptan *et al.*, 2010; Abraham *et al.*, 2019; Rajan *et al.*, 2013; Dinaharan *et al.*, 2011; Kalaiselvan *et al.*, 2014).

The matrix metal is a comparatively soft material with unique mechanical and physical properties. The various matrix materials like aluminum, copper, magnesium, and titanium are relatively soft materials with good ductility, machinability, malleability, and thermal and electrical conductivity. The choice of matrix is based on strength to weight ratio, ease of handling, and other merits that may also apply depending on the purpose of application (Boostani *et al.*, 2015). A few metals have appreciable applications as matrix components in structural composite design with commendable achievements (Dinaharan *et al.*, 2011). The matrix serves two main objectives in matrix-based structural composites: Holding the reinforced elements in balance and deforming to transfer force among all the individual reinforced components. The main functions of the matrix are to hold the reinforcement, preserving the integrity of the reinforcement, resisting the formation of crack propagation or growth, and enhancing the fracture resistance of the MMCs (Selvam *et al.*, 2013; Esawi *et al.*, 2010; Wang *et al.*, 2010; Yadav and Bauri, 2010a,b).

The reinforced material that has a good bonding and that strengthens the matrix material is called reinforcement. The reinforcement can be very hard and robust, yet very light in weight. Strength-to-weight and stiffness-to-weight ratios are several times higher than the matrix materials. The reinforcement can be continuous or discontinuous fibers and particles. This reinforcement is also used to enhance physical characteristics of the matrix material such as wear resistance, corrosion resistance, stiffness, Young's modulus, heat conduction or resistance, and strength (Dinaharan *et al.*, 2011). A reinforcement that enhances the toughness of the matrix has to be stronger and stiffer than the matrix, capable of influencing the mechanism of failure to the benefit of the composite. The common content of ceramic particles used as traditional reinforcements are silicon carbide (SiC), boron carbide (B₄C), aluminum oxide (Al₂O₃), and titanium carbide (TiC) (Shirvanimoghaddam *et al.*, 2016b). Table 1 shows the various properties of ceramic reinforcements.

The factors to be taken into account for the selection of reinforcement are compatibility with matrix material, thermal stability, density, melting temperature, final application, etc., (Gangil *et al.*, 2017). The reinforcement's compatibility, density, chemical and thermal stability with matrix material is essential for material manufacturing and end-use. The difference in thermal coefficient between matrix as well as reinforcement is a significant composite parameter used in thermal cycling (Reddy *et al.*, 2011). It is a function of difference between matrix and reinforcement thermal expansion coefficients and strengthens the dislocations within the composite. Selected manufacturing method and reinforcement affect the crystal structure of the fabricated MMCs.

Matrix Material

The matrix materials are aluminum, magnesium, copper, titanium, iron and alloys which offer compatible assistance to reinforcement and used in structural components. The reinforcement provides the composite's strength and rigidity. The matrix cannot bear much of the load (Dobrzański *et al.*, 2014; Ahamed and Senthilkumar, 2010; Das *et al.*, 2010). The matrix connects with the reinforcement together and distributes the load evenly to reinforced particles. A healthy matrix needs to occupy between the reinforcements and form a good interface bond (Roy *et al.*, 2012). It also offers ductility, protects the fibers against corrosion, and prevents the expanding of cracks within the matrix. The matrix selected should be flexible and it will help prevent reinforcement collapsing under tensile or compressive load applied (Dinaharan *et al.*, 2011). It is also vital that there is no possibility of a chemical reaction between matrix material and reinforcement and that the matrix material does not damage the reinforcement (Kumar and Murugan, 2012).

Table 1 Properties of various ceramic reinforcements

Reinforcement material	Density (Kg m ⁻³)	Melting point (K)	Thermal conductivity (W m ⁻¹ K ⁻¹)	Thermal coefficient expansion (x 10 ⁶ /K)	Vickers hardness (Hv)	Young's modulus (GPa)
SiC	3200	3073	270	5.1–5.8	2800	560
B ₄ C	2520	2780	32.5	7.3	1855	472
Al ₂ O ₃	3855	2323	29	8.5	1780	460
TiC	4770	3413	31.8	7.6	2270	450

Table 2 The mechanical properties of various wrought and cast aluminum alloys

Aluminum alloys series	Composition	yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Vickers hardness (HV)
1xxx	Al	70–150	90–165	10–40	25–44
2xxx	Al–Cu	90–330	170–420	16–24	80–115
3xxx	Al–Mn	60–115	90–155	10–26	30–45
4xxx	Al–Si	70–180	110–250	8–20	30–55
5xxx	Al–Mg	60–260	170–330	15–35	60–95
6xxx	Al–Mg–Si	55–290	100–370	10–30	60–105
7xxx	Al–Zn–Cu	170–390	230–575	3–10	50–165

Aluminum Alloys

Aluminum is the most easily available metal in the world and the third most popular metal. Aluminum's adaptability provides it an even more-used metal after steel. Pure aluminum is soft, ductile, corrosion resistant, and highly electrically conductive. However, alloying with other components is vital and provides greater strength for other applications. Aluminum is one of the softest engineering metals with a superior strength-to-weight ratio to steel. Aluminum's main alloying components are copper, magnesium, silicon, manganese, nickel, and zinc (Mondolfo, 2013). The mechanical properties of the wrought and cast aluminum alloys are shown in Table 2. All these are used to enhance the strength of pure aluminum. The primary categories of aluminum alloys are the following:

- 1xxx series (Al) are commercially pure aluminum;
- 2xxx series (Al–Cu) are high-strength materials primarily used in the aviation sector;
- 3xxx series (Al–Mn) primarily used in the canning industry;
- 4xxx series (Al–Si) primarily used in welding rods and brazing sheet;
- 5xxx series (Al–Mg) used unprotected for structural and architectural purposes;
- 6xxx series (Al–Mg–Si) are the most popular extrusion alloys used in the automobile sector; and
- 7xxx series (Al–Zn–Cu) are high-strength materials primarily used in the aviation sector.

Magnesium Alloys

Magnesium is the softest metal in use, with a density of 1.7 g cm⁻³. The melting point of magnesium is 650°C and has a hexagonally closed pack (HCP) structure. The thermal conductivity of magnesium is lower than that of aluminum, but coefficient of thermal expansion (CTE) is nearly the same. Alloying can substantially improve Mg's properties and most frequently used alloy ingredients are Al, Zn, Mn, and Zr. Magnesium and its alloys are used in many applications such as auto components, sports products, energy instruments, aviation machinery as they weigh less, have good machinability, and are easy to cast. The disadvantage of using pure magnesium is that it is extremely susceptible to corrosion (Avedesian and Baker, 1999). The mechanical properties of the wrought and cast magnesium alloys are shown in Table 3.

Copper and Alloys

Copper is one of the earliest metals discovered by man. The copper tubing used in water plumbing in pyramids was found to be in a serviceable condition even after 5000 years. Copper has face-centered cubic (FCC) structure. Pure copper is a high ductile metal having good electrical and thermal conductivity and is also corrosion resistant. Pure copper is soft, malleable, and difficult to machine. Because of its high electrical conductivity (only silver and gold are better), it is used extensively in various electrical applications. Copper is an excellent thermal conductive metal, which makes it suitable for high-temperature applications. The widespread use of electronic parts in automobiles raises the quantity of copper used per vehicle (Davis, 2001). The primary categories of copper alloys are the following:

Table 3 Mechanical properties of various categories of magnesium wrought and cast alloys

<i>Magnesium alloys series</i>	<i>Density ($g\ cm^{-3}$)</i>	<i>Tensile strength (MPa)</i>	<i>Yield strength (MPa)</i>	<i>Elongation (%)</i>	<i>Vickers hardness (HV)</i>
AZ91	1.81	240	165	3	70
AM60	1.80	220	130	8	65
AS41	1.77	215	140	6	55
AE44	1.82	245	142	10	62
AJ62	1.8	235	140	10	62
ZM21	1.8	200	124	9	55
AZ80	1.8	330	230	12	70

- C1xxx series (Cu) are commercially available pure copper, primarily used in electrical components;
- C2xxx series (Cu–Zn) are high strength materials used in automobile and defense sector;
- C3xxx series (Cu–Zn–Pb) alloys are good for cold-working and used in electrical components;
- C4xxx series (Cu–Zn–Sn) alloys have good corrosion-resistance properties;
- C5xxx series (Cu–Sn) alloys have high fatigue strength and used for making springs;
- C6xxx series (Cu–Al) alloys are used in the automotive and shipbuilding industries; and
- C7xxx series (Cu–Ni) alloys are used in high-temperature applications.

Nickel and Alloys

Nickel is always an essential metal for a broad number of sectors, probably as it is a highly flexible metal that alloys with almost all other metals. Nickel has FCC structure and is a good ductile metal. Nickel alloys withstand elevated stresses and temperatures, allowing them to be used for extremely high-performance applications like in jet engine blades. Nickel and its alloys have excellent corrosion resistance, high density, and excellent magnetic and electronic properties. The alloy sequence of nickel–chromium and nickel–chromium–iron resulted in increased strength and used in high-temperature applications (Thompson, 2000).

Titanium and Alloys

Titanium is a low-density material (approximately 60% of the density of steel and superalloys) that can be strengthened greatly by alloying and deformation processing. Titanium has two crystal structures. Pure titanium at room temperature is HCP, known as “alpha” (α) titanium. At 883°C the alpha phase transforms into a body-centered cubic (BCC) phase known as “beta” (β) titanium. Alpha alloys contain elements such as aluminum and tin, which stabilize the structure. The alpha titanium alloys have better creep properties than beta alloys and are preferred for high-temperature applications. The aging treatment results in the precipitation of alpha, giving a matrix of both α and β phases. Beta alloys contain ingredients such as vanadium, niobium, and molybdenum which decrease the temperature required for the β phase change, thus promoting the formation of β . These alloys have excellent forgeability over a wide range of forging temperatures. The admirable corrosion resistance and biocompatibility coupled with good strengths make titanium and its alloys useful in petrochemical, marine environments, and biomaterials application. Pure titanium is nontoxic; commercially pure titanium and some titanium alloys generally are biologically compatible with human tissues and bones (Bache, 2003).

Iron and Alloys

Iron can be found readily in the crust of the earth, but pure iron is not so a helpful material as it readily rusts. It also has such a high melting point that casting cannot shape it readily. Cast iron is the most commonly used metal, accounting for 95% of metal manufacturing worldwide. Its low price and high strength make it indispensable in engineering applications such as machine and machine tool building, automobiles, big ship hulls, and building structural elements. Manganese, copper, aluminum, titanium, magnesium, chromium, molybdenum are the main alloying components in iron. Adding vanadium and zirconium to iron improves its mechanical characteristics (Mbuya *et al.*, 2003).

Reinforcements

Ceramic materials are inorganic and non-metallic materials. Ceramic materials can be crystalline or crystalline to a certain extent. Clay was one of the oldest ceramic materials used for pottery, but now many distinct ceramic materials are being used in industrial and construction goods (Liu *et al.*, 2013). Ceramics are classified according to their compositions as oxides, carbides, nitrides, and borides (Das *et al.*, 2010). Advanced ceramics are developed and manufactured to be used in electrical components, body-worn armor and in high-temperature applications. Ceramic materials tend to be strong, fragile, rigid, chemically inert, and non-conductors of heat and electricity. But their characteristics differ extensively (Xiu *et al.*, 2012; Mondolfo, 2013; Avedesian and Baker, 1999;

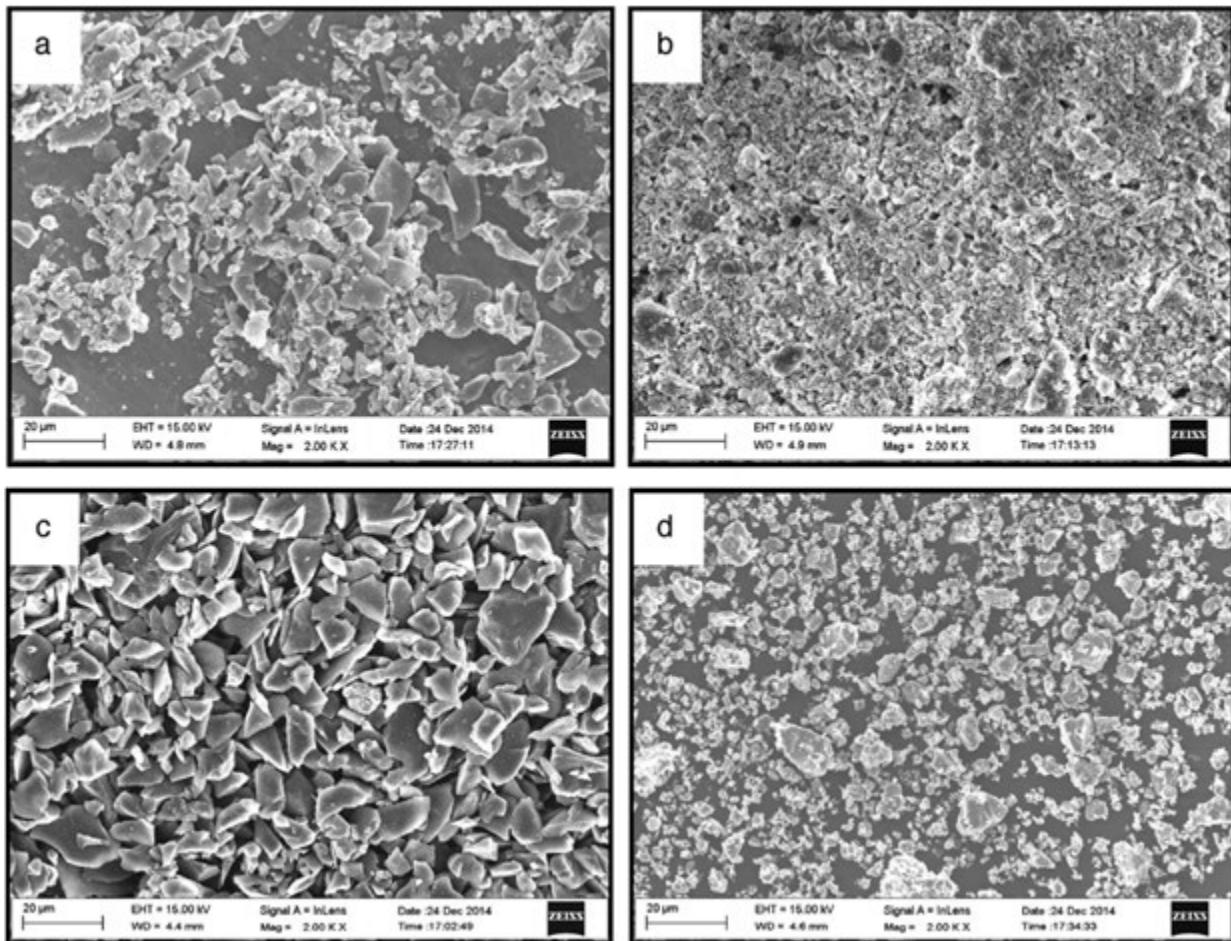


Fig. 1 FESEM micrograph of ceramic particles: (a) SiC, (b) Al_2O_3 , (c) B_4C , and (d) TiC. Reproduced from Dinaharan, I., 2016. Influence of ceramic particulate type on microstructure and tensile strength of AA6082 aluminum matrix composites produced using friction stir processing. *Journal of Asian Ceramic Societies* 4, 209–218.

Davis, 2001). The materials used for the reinforcement in MMCs are typically ceramics because they possess rigidity, hardness, and comparatively low density in a desirable form. The potential reinforcement material includes SiC (Shorowordi *et al.*, 2003), Al_2O_3 (Shorowordi *et al.*, 2003), B_4C (Shorowordi *et al.*, 2003), TiC (Lijay *et al.*, 2016), TiB_2 (Rajan *et al.*, 2013), graphite (Moghadam *et al.*, 2015), etc. The morphology and size of the reinforced particles also determine the mechanical properties of the reinforcement during the fabrication of MMCs. The reinforcement is designed to give greater stiffness and strength to the matrix alloy (Shorowordi *et al.*, 2003; Lijay *et al.*, 2016; Shirvanimoghaddam *et al.*, 2016a).

Ceramic Particles

Silicon carbides

Silicon carbide (SiC) is a hard covalently bonded material. SiC compound consists of a silicon (Si) atom and four carbon (C) atoms which are covalently bonded between two of them. Silicon carbide (SiC) is a non-oxide ceramic engineering material that has gathered a considerable amount of interest. The SiC particles pose a relatively low thermal expansion, high thermal conductivity, high hardness, and resistance to abrasion and corrosion. The SiC particle retains its elastic resistance even up to a temperature of 1650°C , which leads it to a wide range of industrial applications at elevated temperatures. When these SiC particles are embedded in MMCs, it certainly improves the overall strength of the composite along with corrosion and wear resistance. The SEM micrograph of typical silicon carbide particles is shown in Fig. 1(a) (Dinaharan, 2016).

Aluminum oxide

Aluminum oxide (Al_2O_3) is called as alumina. Alumina is a white powder-like table salt. It has a high melting temperature above 2050°C and is chemically stable. Regular alumina is produced from bauxite by the Bayer process (invented by Bayer). When bauxite ore is dissolved in sodium hydroxide solution, the bauxite converts into sodium aluminate and the impurities removed as slag is known as red mud. Al_2O_3 particles are separated at 1100°C by hydrolyzing process from the sodium aluminate particles.

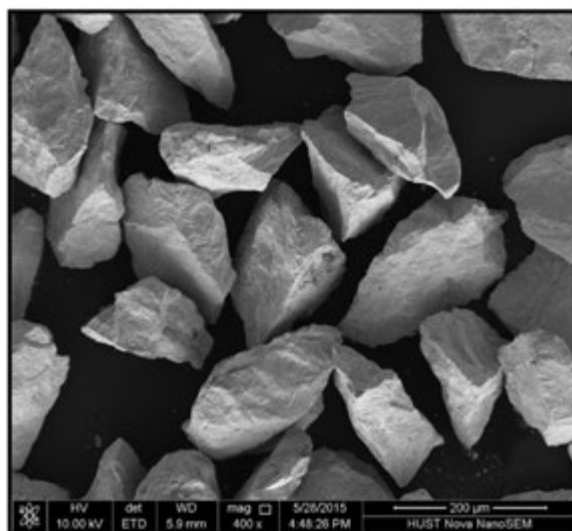


Fig. 2 The morphology of the used WC particles. Reproduced from Liu, J., Yang, S., Xia, W., Jiang, X., Gui, C., 2016. Microstructure and wear resistance performance of Cu–Ni–Mn alloy based hardfacing coatings reinforced by WC particles. *Journal of Alloys and Compounds*, 654, 63–70.

The SEM micrograph of aluminum oxide particles is shown in [Fig. 1\(b\)](#). Alumina allows it to be used for a wide range of applications due to its high hardness, capability of operating at elevated temperatures, and strong electrical insulation ([Dinaharan, 2016](#); [Su et al., 2012](#)).

Boron carbide

Boron carbide (B_4C) is a high-performance ceramic particle that has low density, a large degree of chemical inertness, thermal stability at elevated temperatures, and outstanding thermo-electrical characteristics ([Kalaiselvan et al., 2014](#)). The extra hardness of boron carbide provides it the surname “black diamond.” B_4C ceramic particles are produced by carbothermal reduction process of boron oxide (B_2O_3) and carbon in an electric arc furnace. The morphology of typical B_4C particles is portrayed in the SEM micrograph shown in [Fig. 1\(c\)](#) ([Dinaharan, 2016](#)). B_4C particles have outstanding physical and mechanical properties such as a high melting point and hardness, good strength to abrasion, high impact strength, excellent chemical resistance, and high absorption capacity for neutrons ([Suri et al., 2010](#)).

Titanium carbide

Titanium carbide (TiC) has a high melting point (3160°C) and is an extremely challenging ceramic material. Typical SEM micrograph of titanium carbide particles is shown in [Fig. 1\(d\)](#) ([Dinaharan, 2016](#)). TiC particles are synthesized using the carbothermal reduction process of titanium dioxide (TiO_2) powder and carbon in an electric arc furnace. Titanium carbide’s main uses are in the production of wear-resistant instruments, slicing instruments, abrasive steel bearings, wear-resistant tools, improving conductivity, and as a nucleating agent ([Parashivamurthy et al., 2001](#)).

Tungsten carbide

Tungsten carbide is often known as a hard metal owing to its high hardness compared to other ceramic powders. Tungsten carbide has a high melting point of 2870°C . Tungsten carbide is synthesized by chemical reaction between tungsten metal and carbon at $1850\text{--}2000^\circ\text{C}$. The SEM micrograph of the tungsten carbide powder is shown in [Fig. 2](#). Tungsten carbide (WC) is a highly desirable material due to its attractive mechanical, physical, and chemical properties such as high hardness, high melting point, good electrical and thermal conductivity, and high corrosion resistance ([Liu et al., 2016](#)).

Nitride particles

Aluminum nitride (AlN) and boron nitride (BN) are having a wide range of industrial applications and the best materials to be used where high thermal conductivity is required. AlN and BN ([Kvashnin et al., 2019](#)) are ideal heat sink materials. AlN is a synthetic ceramic particle with a unique combination of useful thermal and electrical properties ([Kumar and Murugan, 2012](#)). Al–SiC and Al–AlNp composites are widely used in microelectronic devices. Although the thermal conductivity of AlN ($175\text{ W m}^{-1}\text{ K}^{-1}$) is less than SiC ($250\text{ W m}^{-1}\text{ K}^{-1}$), AlN is chemically more stable than SiC. Aluminum does not react with AlN ([Kumar and Murugan, 2012](#)), whereas in Al–SiC composites Al_4C_3 phase is formed by the reactions of Al with SiC and degrades the mechanical properties of Al–SiC composite ([Pei et al., 2015](#)). AlN has good compatibility with Al alloy, excellent thermophysical properties, good interfacial adherence without any interfacial reaction ([Kumar and Murugan, 2012](#)), high specific strength and stiffness, high thermal conductivity, high electrical resistivity, low dielectric constant and tailorable coefficient of thermal expansion. Thus Al–AlNp composite is an ideal candidate material for electronic packaging materials ([Kumar and Murugan, 2012](#)).

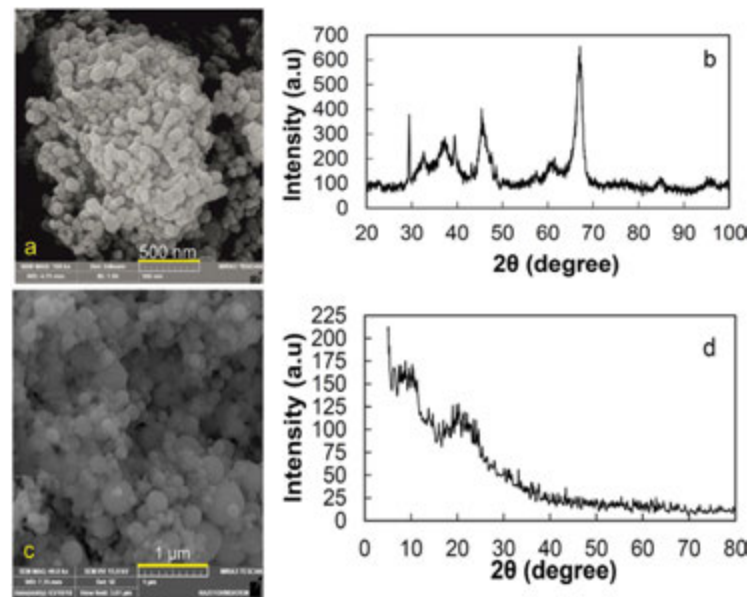


Fig. 3 The morphology and XRD pattern of (a, b) nano-sized Al_2O_3 and (c, d) nano-sized SiO_2 . Reproduced from Jalilvand, M.M., Mazaheri, Y., Heidarpour, A., Roknian, M., 2019. Development of A356/ Al_2O_3 + SiO_2 surface hybrid nanocomposite by friction stir processing. *Surface and Coatings Technology*, 360, 121–132.

Nanoceramic powders

Ceramic nanocomposites are being increasingly used in the development of new processing techniques that enable to fabricate products to range from the laboratory study to the commercial level. The nanoparticles can be produced using high energy ball milling process. The mass production of nano-size particles can be produced using mechanical milling process and are also economical (Dindarsafa *et al.*, 2017). The kinetic energy produced during the milling process is transferred to powder from the ball during milling process (Dindarsafa *et al.*, 2017). The transfer of kinetic energy is governed by many factors, like the types of mill, the powder used during milling, speed, size of the balls, dry or wet milling, temperature of milling, and the duration of milling. These nanoparticles reinforced into MMCs enhances the yield stress and microhardness of the fabricated composites. Further refining of the grain size can contribute to lower the yield stress.

Jalilvand *et al.* (2019) fabricated nano-sized $\alpha\text{-Al}_2\text{O}_3$ and SiO_2 powders as reinforcements to produce the A356/ Al_2O_3 + SiO_2 hybrid composite. The morphology and XRD pattern of the nano-sized Al_2O_3 and SiO_2 particles are shown in Fig. 3. The microstructural examination confirmed that reinforcement powders were uniformly distributed in the matrix. The authors confirmed that adding nano-sized Al_2O_3 and SiO_2 materials increase the microhardness of the hybrid surface composite by around 40%.

In their research work, Rajabi and Ghazali (2017) synthesized nanoparticles by the processing of micron-level Al_2O_3 and SiO_2 particles using high energy ball mill to nano-size particles. The author's ball-milled Al_2O_3 and SiO_2 particles after 1, 5, 10, 15, 20 and 25 h of milling using Fritsch Pulverisette-6 planetary ball mill with a fixed rotational speed of 300 rpm. The ball-milled particles were analyzed using particle size analyzer and distribution was measured using Malvern (Zetasizer Nano zs). The FESEM micrographs of morphological behavior of the as-milled TiC powders at (a) 1 h, (b) 5 h, (c) 10 h, (d) 15 h, (e) 20 h, and (f) 25 h milling are shown in Fig. 4.

Industrial Residue Particles

MMCs have a wide variety of benefits over monolithic alloys including high strength, elastic modulus, stiffness, creep resistance, reduced density, and low strength-to-weight ratio making them efficient structural materials. But over the last few decades, their large production price has confined the usage of MMCs (Vencl *et al.*, 2010; Ravindran *et al.*, 2013; Kumar *et al.*, 2017). However, cost-effective and industrial residue particles such as fly ash, rice husk ash, bamboo ash, coconut shell ash, etc., have been developed to widen the MMC's applications (Selvam *et al.*, 2013).

Fly ash particles

Fly ash materials that are by-products of waste are generated during coal combustion by thermal power plants and pose a serious ecological issue in connection with their processing and recycling. Most non-combustible carbon fractions consist of clay minerals, which respond and float during combustion at the flame temperature to create a large and diverse mixture of strong (precipitator) or void (cenosphere) spherical objects with a density of 1.6–2.3 and 0.4–0.6 g cm^{-3} , simultaneously. The chemical composition of Type C and Type F fly ash are shown in Table 4. Type C is used in addition to cement because of its elevated CaO concentration.

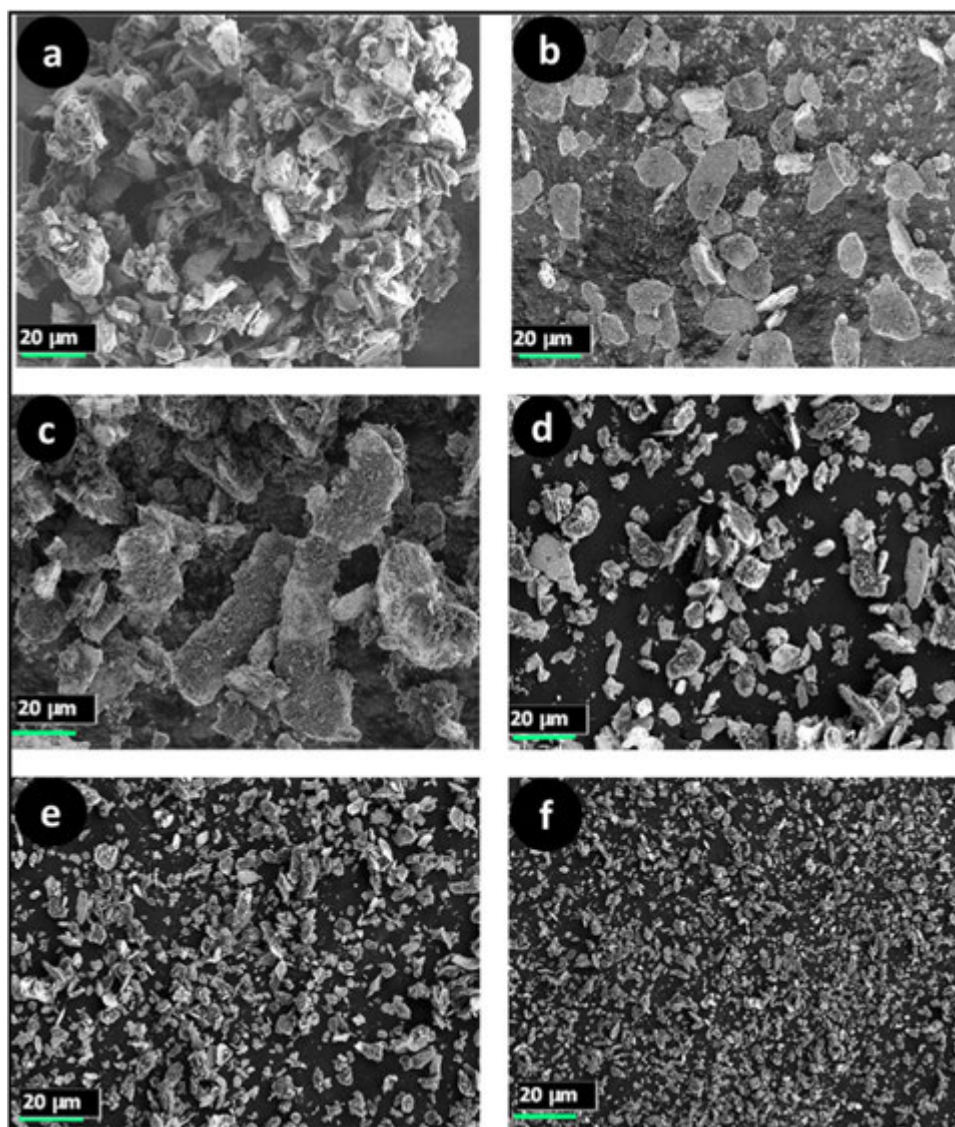


Fig. 4 FE-SEM micrographs of morphological behavior of the as-milled TiC powders at (a) 1 h, (b) 5 h, (c) 10 h, (d) 15 h, (e) 20 h, and (f) 25 h milling. Reproduced from Rajabi, A., Ghazali, M.J., 2017. Quantitative analyses of TiC nanopowders via mechanical alloying method. *Ceramics International* 43 (16), 14233–14243.

Table 4 Shows the chemical composition of various types of fly ash

Chemical composition wt%	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	TiO_2	MnO_2	C
Fly ash	63.95	26.07	4.88	0.02	0.04	2.43	0.68	0.02	1.91
Calcined fly ash at 900°C for 30 min	67.54	23.75	4.45	0.16	0.21	3.57	0.22	0.02	0.08

Note: Reproduced from Escalera-Lozano, R., Gutiérrez, C.A., Pech-Canul, M.A., Pech-Canul, M.I., 2007. Corrosion characteristics of hybrid Al/SiCp/MgAl₂O₄ composites fabricated with fly ash and recycled aluminum. *Materials Characterization* 58 (10), 953–960.

Type F is more appropriate for MMC production (Zhang *et al.*, 2009). Dinaharan *et al.* (2016) fabricated fly ash reinforced AA6061 aluminum composites using friction stir processing (FSP). The SEM micrograph portraying the morphology of cenospheres fly ash is shown in Fig. 5. The reinforced fly ash particles refine the grain size during FSP. The incorporation of fly ash particles to the AA6061 aluminum matrix increased the microhardness and wear resistance of the fabricated composite.

Escalera-Lozano *et al.* (2007) fabricated Al/SiCp/spinel hybrid composites fabricated with SiCp, cenosphere type fly ash (FA) and recycled aluminum by the liquid-state route. The cenosphere is shown in Fig. 6. The formation of Mg-spinel was controlled by the presence of cenosphere fly ash. The formation of Mg₂Si is a critical parameter to avoid aggressive localized corrosion.

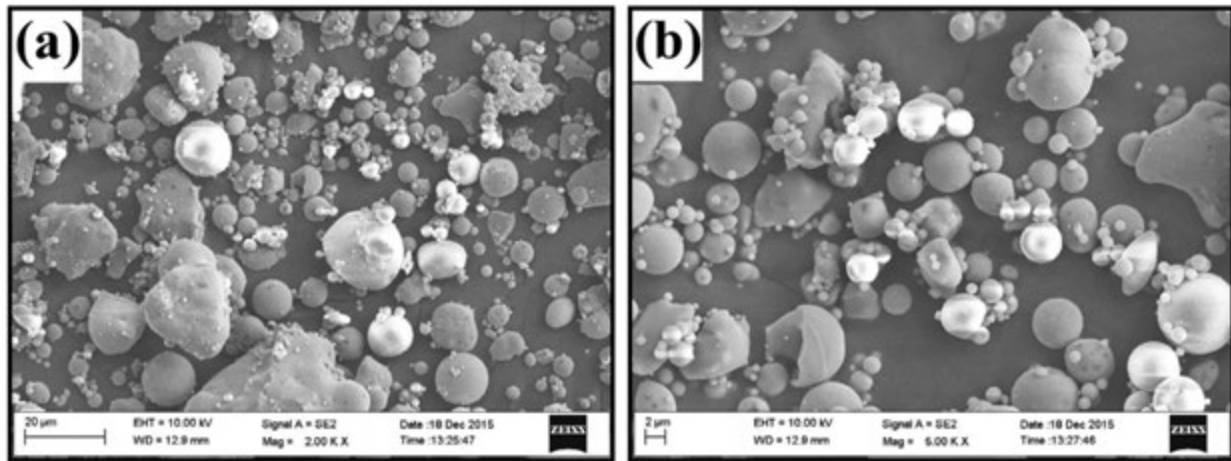


Fig. 5 FESEM micrograph of fly ash particles at magnification: (a) 2000x and (b) 5000x. Reproduced from Dinaharan, I., Nelson, R., Vijay, S.J., Akinlabi, E.T., 2016. Microstructure and wear characterization of aluminum matrix composites reinforced with industrial waste fly ash particulates synthesized by friction stir processing. *Materials Characterization* 118, 149–158.

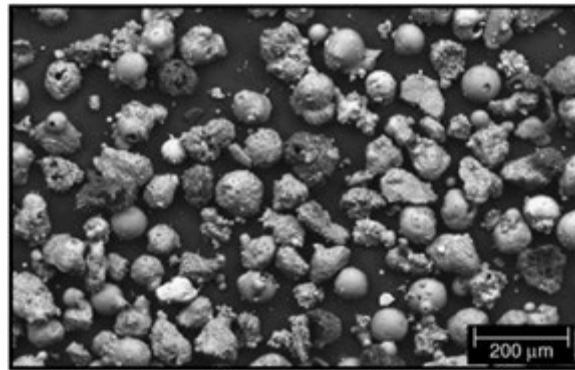


Fig. 6 SEM photomicrograph showing the typical morphology of the cenospheres fly ash. Reproduced from Escalera-Lozano, R., Gutiérrez, C.A., Pech-Canul, M.A., Pech-Canul, M.I., 2007. Corrosion characteristics of hybrid Al/SiCp/MgAl₂O₄ composites fabricated with fly ash and recycled aluminum. *Materials Characterization* 58 (10), 953–960.

Rice husk ash particles

Rice milling produces a bi-product known as husk. Rice husk is a farm residue that represents 20% of the world's grain generated each year. The dumping of rice hull ash pollutes the soil and its surroundings. If the husk is burned below 800°C under controlled temperature, primarily in an amorphous form can produce ash with silica. The chemical composition of rice husk ash is given in [Table 5](#). The rice husk ash (RHA) is cost effective than other reinforcement materials like SiC, Al₂O₃, B₄C and TiC ([Gladston et al., 2015](#)). [Dinaharan et al. \(2017\)](#) fabricated pure copper matrix composite reinforced with rice husk ash using FSP. The SEM micrograph portraying the morphology of rice husk ash is shown in [Fig. 7](#). The addition of rice husk ash to copper matrix enhanced microhardness and tribological behavior of the copper matrix composite.

Bamboo leaf ash particles

Bamboo leaf is a residue that represents 6% of the world's residue generated each year. The usage of bamboo leaf ash as a strengthening product in the production of MMCs is economically feasible. In the laboratory, by preserving the bamboo leaves in an electric furnace at 600°C calcining temperature for 2 h, bamboo leaf ashes were obtained. The ashes were ground once calcinated and sieved ([Bahrami et al., 2016](#)). The chemical composition of bamboo leaf ash is given in [Table 6](#). [Kumar and Birru \(2017\)](#) used bamboo leaf ash as a reinforcement to fabricate Al–4.5%Cu composite using stir casting furnace. The SEM micrograph portraying the morphology of bamboo leaf ash is shown in [Fig. 8](#). The fabricated Al–4.5%Cu composite exhibits a higher hardness and tensile strength after being reinforced with bamboo leaf ash.

Coconut shell ash particles

The coconut shell regarded as an agro scrap is present in huge quantities in tropical regions of India and around the globe. Developing metal matrix composites using coconut shell ash as a reinforcing ingredient is an economically feasible option for

Table 5 Chemical composition of rice husk ash

SiO_2	Al_2O_3	C	CaO	MgO	K_2O	Fe_2O_3	LOI^a
90.23	3.54	1.23	1.58	0.53	0.39	0.21	2.29

^aLOI – Loss on Ignition.

Note: Reproduced from Dinaharan, I., Kalaiselvan, K., Akinlabi, E.T., Davim, J.P., 2017. Microstructure and wear characterization of rice husk ash reinforced copper matrix composites prepared using friction stir processing. Journal of Alloys and Compounds 718, 150–160.

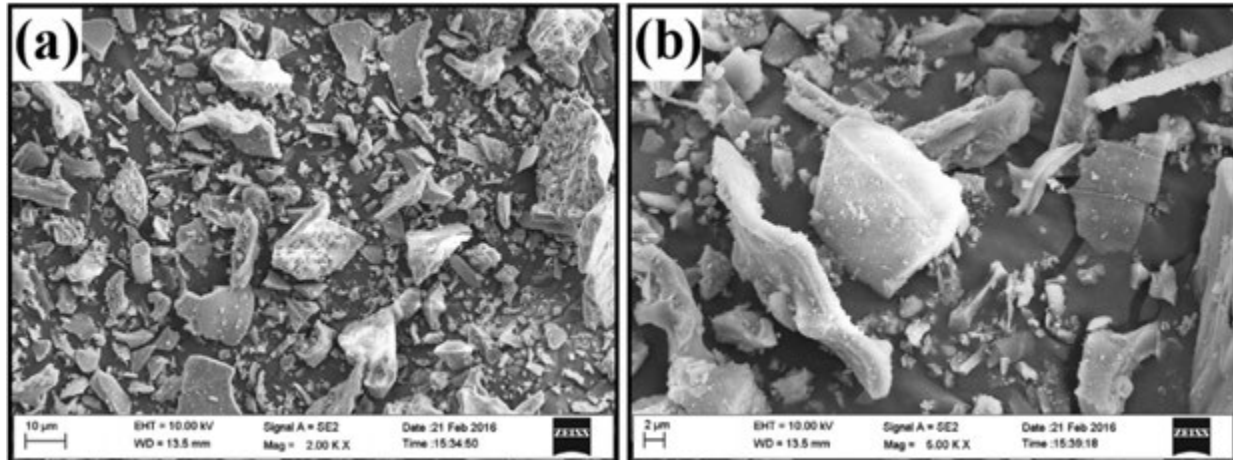


Fig. 7 SEM micrograph of RHA particles at magnification: (a) 2000x and (b) 5000x. Reproduced from Dinaharan, I., Kalaiselvan, K., Akinlabi, E. T., Davim, J.P., 2017. Microstructure and wear characterization of rice husk ash reinforced copper matrix composites prepared using friction stir processing. Journal of Alloys and Compounds 718, 150–160.

Table 6 Chemical composition of bamboo leaf ash

SiO_2	CaO	K_2O	C	Al_2O_3	MgO	Fe_2O_3
75.9	6.68	5.62	4.2	4.13	1.85	1.32

Note: Reproduced from Kumar, B.P., Birru, A.K., 2017. Microstructure and mechanical properties of aluminium metal matrix composites with addition of bamboo leaf ash by stir casting method. Transactions of Nonferrous Metals Society of China 27 (12), 2555–2572.

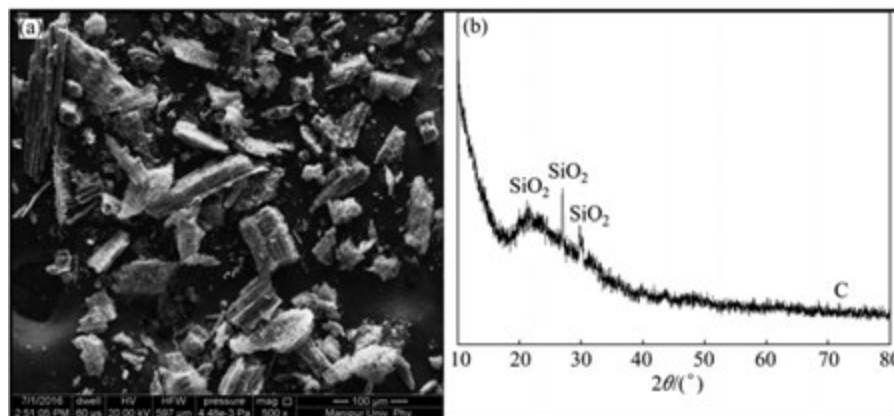


Fig. 8 SEM image of synthesized bamboo leaf ash (a) and XRD pattern (b). Reproduced from Kumar, B.P., Birru, A.K., 2017. Microstructure and mechanical properties of aluminium metal matrix composites with addition of bamboo leaf ash by stir casting method. Transactions of Nonferrous Metals Society of China 27 (12), 2555–2572.

Table 7 Chemical composition of coconut shell ash

SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	CaO	ZnO	MnO
45.36	21.82	18.58	12.32	0.73	0.67	0.32	0.2

Note: Reproduced from Subramaniam, B., Natarajan, B., Kaliyaperumal, B., Chelladurai, S.J.S., 2018. Investigation on mechanical properties of aluminium 7075-boron carbide-coconut shell fly ash reinforced hybrid metal matrix composites. *China Foundry* 15 (6), 449–456.

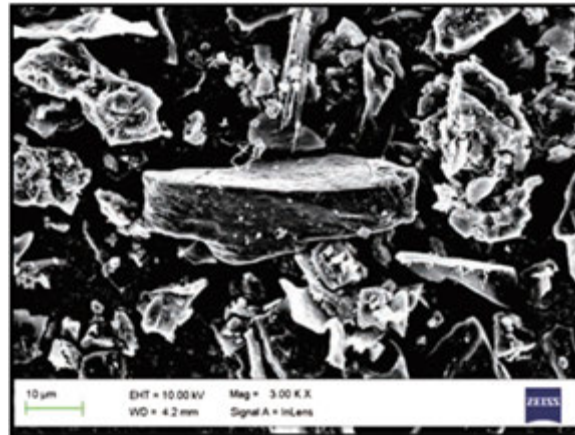


Fig. 9 SEM morphology of coconut shell fly ash powder. Reproduced from Subramaniam, B., Natarajan, B., Kaliyaperumal, B., Chelladurai, S.J.S., 2018. Investigation on mechanical properties of aluminium 7075-boron carbide-coconut shell fly ash reinforced hybrid metal matrix composites. *China Foundry* 15 (6), 449–456.

reducing air pollution, storage and disposal costs. In the laboratory, by preserving the coconut shell in an electric furnace at 850°C calcining temperature for 3 h, coconut shell ashes were obtained (Bahrami *et al.*, 2016). Table 7 shows the chemical composition of the coconut shell ash. Subramaniam *et al.* (2018) used coconut shell ash and B_4C powder as reinforcements for the fabrication of AA7075 aluminum composite using stir casting furnace. SEM micrograph portraying the morphology of coconut shell ash is shown in Fig. 9. The composite exhibits a 33% higher hardness and 66% higher tensile strength over the AA7075 aluminum matrix alloy.

Miscellaneous

Zircon is used in ceramics, specialized castings and diverse refractoriness, due to its elevated heat and abrasion strength. Das *et al.* (2006) fabricated zircon sand/Al–4.5 wt% composite using stir casting furnace. The authors used different sizes of zircon sand particles into the melt for fabricating the composite as shown in Fig. 10. The authors concluded that due to the addition of zircon sand to the matrix, the abrasive wear resistance of the zircon sand/Al–4.5 wt% composite was enhanced. Red mud is a significant insoluble residue material produced by Bayer's process during alumina manufacturing from bauxite. The presence of significant oxides such as Al_2O_3 , TiO_2 , Fe_2O_3 , and Na_2O in red sand, low cost and easy accessibility have made it a significant reinforcement material for the production of MMCs (Sharma *et al.*, 2018). Table 8 provides the chemical composition of red mud.

Intermetallics

In recent years, material scientists and metallurgists have drawn more attention to the increasing need for new materials with specific properties and applications. Some intermetallic compounds such as aluminides in titanium and nickel which have greater strength, reduced density, greater cracking strength, and greater modulus than standard alloys have a serious concern in processing and characteristics. Intermetallic aluminum-rich materials such as Al_3Ti , Al_3Zr , Al_3Fe , Al_3Ni , Al_2Cu , and Al_3C_4 are used to reinforce aluminum matrix composites (AMCs) since they have low density and thermal coefficients of expansion, high modulus, and melting temperatures and strong recycling behavior (Dinaharan, 2018). One of the significant engineering materials of the present era is particulate-reinforced AMC. The fabrication of AMCs can be classified as liquid and solid metallurgy route. The liquid metallurgy route is easy and cost-effective compared with solid metallurgy route. Liquid metallurgy processing requires either introducing reinforcement particles directly to the liquid metal or synthesizing them in the melt. The former is regarded as ex-situ processing, while the latter is called in-situ processing. In-situ manufacturing benefits include fine size reinforcement materials, strong interfacial bond strength, uniform particle dispersal, thermodynamically stable particles, and reduced processing costs (Wang *et al.*, 2010). Intermetallic components can be synthesized easily by exothermic reactions within the molten aluminum (Dinaharan, 2018).

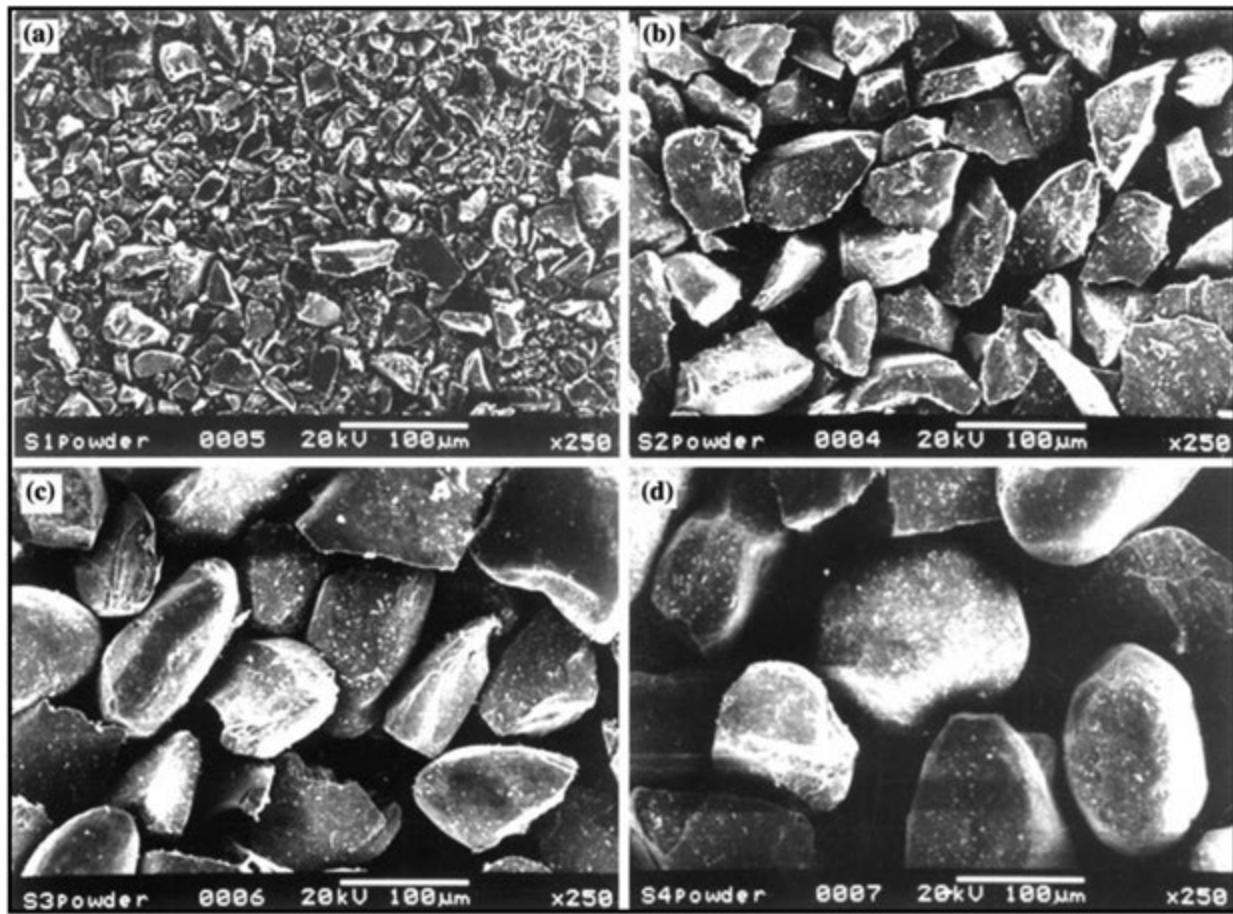


Fig. 10 Scanning electron micrographs of zircon particles of average size (a) 15 μm , (b) 65 μm , (c) 90 μm , and (d) 135 μm . Reproduced from Das, S., Udhayabanu, V., Das, S., Das, K., 2006. Synthesis and characterization of zircon sand/Al-4.5 wt% Cu composite produced by stir casting route. *Journal of Materials Science* 41 (14), 4668–4677.

Table 8 Chemical composition of red mud

Al_2O_3	Fe_2O_3	SiO_2	TiO_2	Na_2O	CaO	LOI ^a
17–19	35–36	7–9	14–16	5–6	3–5	10–12

^aLOI – Loss on Ignition.

Note: Reproduced from Sharma, A., Belokar, R.M., Kumar, S., 2018. Dry sliding wear characterization of red mud reinforced aluminium composite. *Journal of the Brazilian Society of Mechanical Sciences and Engineering* 40 (6), 294.

Al₃Ti particles

Compared to most other inter-metallic-rich aluminum products, Al_3Ti is a very interesting reinforcement because of its higher melting point ($\sim 1623\text{K}$) and a relatively low density (3.4 gm cm^{-3}). The experimental techniques are to melt the aluminum in a furnace and add K_2TiF_6 at the same temperature for a holding time of 30 min (Dinakaran, 2018). The chemical reactions that form Al_3Ti using aluminum and K_2TiF_6 are provided in equation, respectively.

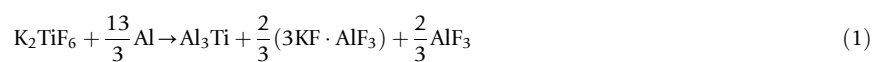


Fig. 11. clearly highlights the presence of flaky Al_3Ti particulates. It is obvious from **Fig. 11** that larger the reinforcing particles are the stronger is their ability to nucleate the Al-grains which results in smaller particles being pushed into the limits of the Al-grain boundaries during the solidification process. This distinctive microstructure is highlighted when LiBF_4 and MgF_2 were used to modify the reinforcing particulate morphology (Wang, *et al.*, 2004).

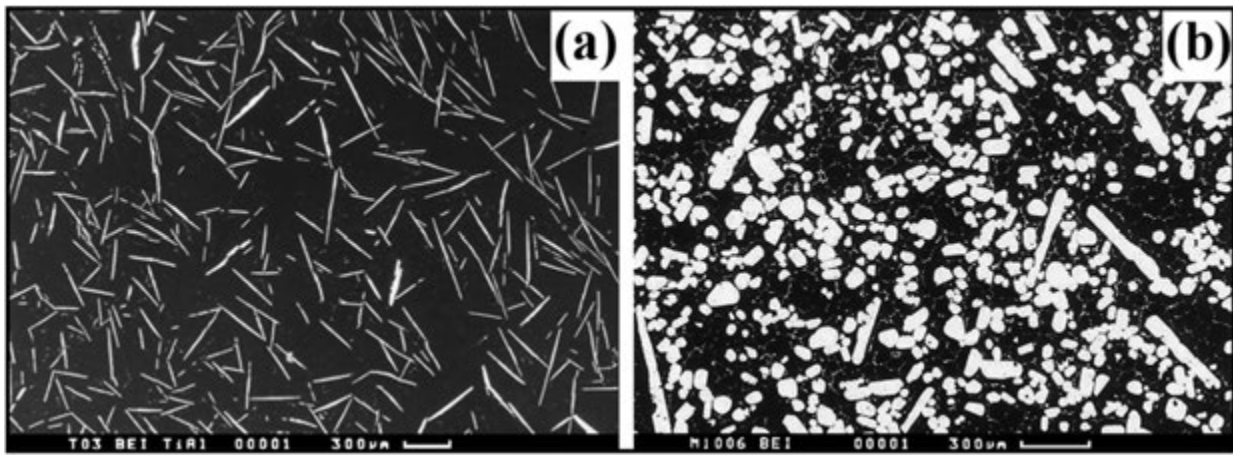


Fig. 11 SEM image of: (a) Flaky Al_3Ti phase, (b) coarsened Al_3Ti particulates in the presence of LiBF_4 and MgF_2 . Reproduced from Wang, X., Jha, A., Brydson, R., 2004. In situ fabrication of Al_3Ti particle reinforced aluminium alloy metal–matrix composites. *Materials Science and Engineering: A* 364 (1–2), 339–345.

Al_3Zr particles

Due to its low density, elevated melting point and competitive elastic (205 GPa) modulus, combined with its oxidation and corrosion resistance, Al_3Zr is regarded to be a prospective candidate for AMC strengthening. Zr addition contributes to the growth of Al_3Zr phase from the melting of aluminum alloy. Due to their high melting temperatures relative to the Al matrix, these particles are consistent and thermally stable (Dinakaran, 2018). Li *et al.* (2011) analyzed the habit and the morphology of the primary Al_3Zr crystals formed during the solidification of Al–1.36 wt% Zr alloy. Al–1.36 wt% Zr alloy was prepared by melting high-purity aluminum (99.999 wt%) and zirconium (99.999 wt%) in an induction furnace. After magnetic stirring and holding at 1100°C for 30 min, it is further stirred mechanically to homogenize the alloy composition. The author analyzed the cast specimen for microstructural study and micrograph shows two typical longitudinal cuts of the primary Al_3Zr crystals and displays one cross-section as shown in Fig. 12(a–c), which has ideal orientation with respect to the microstructure observation planes. It can be seen that the Al_3Zr crystal has a tabular habit. It is found that the shape of the longitudinal cut is size dependent.

Al_2Cu particles

Dinakaran *et al.* (2019) used stir casting furnace to prepare AA2024/ Al_2Cu AMCs. As reinforcement material, measured quantities of copper (Cu) particles were added to molten aluminum to initiate the reaction using a stir casting furnace. The microstructures of Al/(0–15 wt%) Al_2Cu AMCs are revealed in the optical and SEM micrographs in Fig. 13. The cast composite was machined into $50 \times 50 \times 100 \text{ mm}^3$ plates. The reinforcement of Al_2Cu particles enhanced the microhardness and the tensile strength after secondary processing with friction stir processing (FSP).

$\text{Mg}_2\text{Si}/\text{Al}$ particles

Qin *et al.* (2006) used an electrical resistance furnace to fabricate $\text{Mg}_2\text{Si}/\text{Al}$ composite ingots. Commercially available Al–20 wt% Si master alloy (ingot) and pure magnesium (ingot, >98.0% purity) were used for fabricating $\text{Mg}_2\text{Si}/\text{Al}$ composite. The furnace temperature was maintained at $680\text{--}700^\circ\text{C}$ for a holding time of 15 min and poured into a steel die. The specimen was machined for microstructural study. Metallographic specimens were polished through standard routines and examined using scanning electron microscopy (SEM) to see the features of the microstructures of etched samples. The deep etched microstructure of the cast specimen is shown in Fig. 14. The in-situ formed Mg_2Si enhanced the microhardness and tensile strength of the as fabricated composites.

Miscellaneous

Al_3Fe is regarded as a prospective candidate for AMC reinforcement owing to its low density (4 g cm^{-3}), high melting point (1420 K) and good tensile strength (190 GPa) coupled with its resistance to oxidation and corrosion. The Al/ Al_3Fe AMCs are manufactured by in-situ techniques following the same procedure as that of Al/ Al_3Ti AMCs. The Fe component in powder form is used to react with the molten aluminum to synthesize the Al_3Fe phase in molten aluminum. The following equation indicates the chemical reaction to form the Al_3Fe phase (Dinakaran, 2018).



The Al_3Ni intermetallic compound can be used as reinforcement in AMCs because of the high Young's modulus (116–152 GPa) and the high tensile strength (2160 MPa). Ni element powder or porous element is used to react with molten aluminum to synthesize Al_3Ni . The following equation indicates the chemical reaction to form the Al_3Fe phase (Dinakaran, 2018).

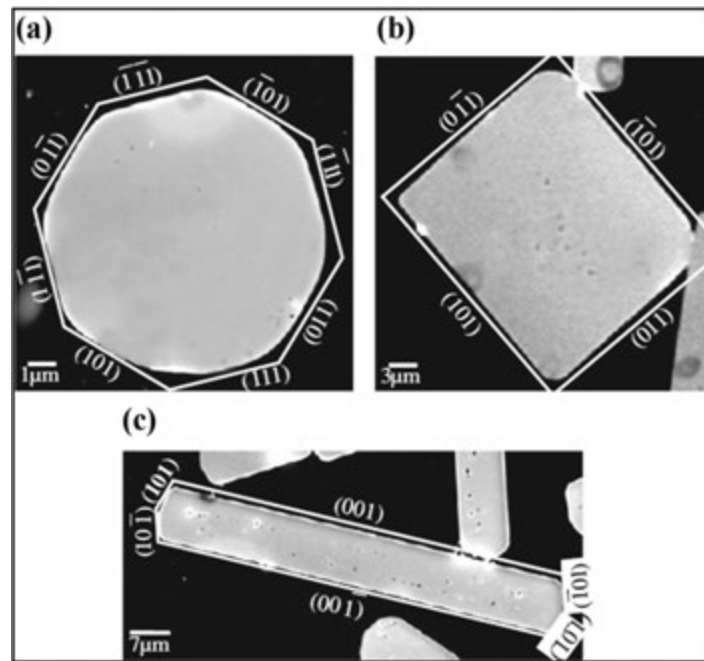


Fig. 12 SEM images showing longitudinal cuts of the primary Al_3Zr crystals in (a) octagonal and (b) rectangular form, and (c) one cross-section of the tabular primary Al_3Zr crystal. Reproduced from Wang, X., Jha, A., Brydson, R., 2004. In situ fabrication of Al_3Ti particle reinforced aluminium alloy metal–matrix composites. *Materials Science and Engineering: A* 364 (1–2), 339–345.

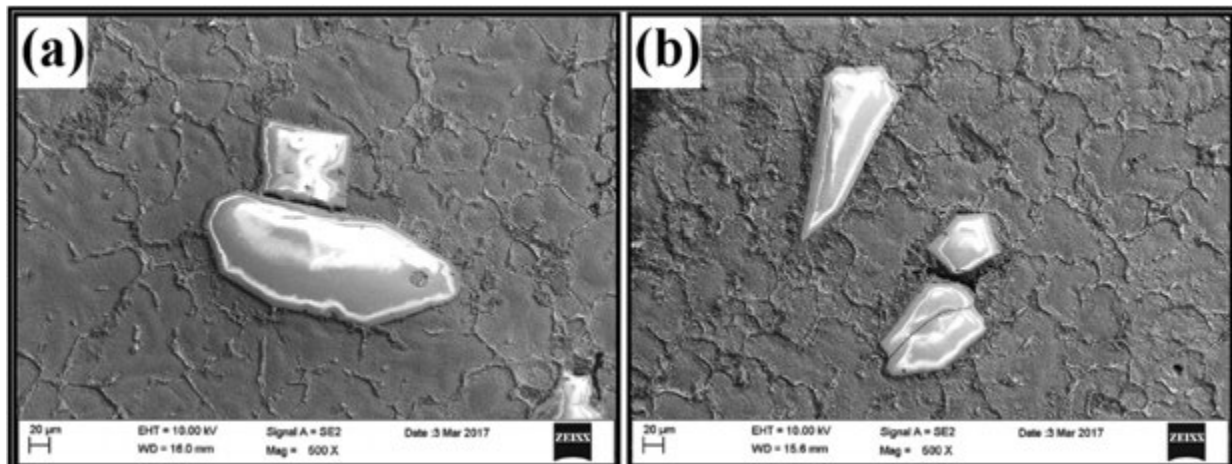


Fig. 13 SEM images showing primary and secondary Al_2Cu particles in the aluminum matrix at: (a) 10 wt% and (b) 15 wt%. Reproduced from Dinaharan, I., Balakrishnan, M., Selvam, J.D.R., Akinlabi, E.T., 2019. Microstructural characterization and tensile behavior of friction stir processed AA6061/ Al_2Cu cast aluminum matrix composites. *Journal of Alloys and Compounds* 781, 270–279.



Metallic Particles

Generally, the most frequently chosen reinforcements are various kinds of ceramic particles, including oxides, borides, carbides, nitrides, etc., when fabricating AMCs. Although the strength of the AMCs increases with the addition of ceramic particles, the resulting AMCs suffer a major loss of tensile ductility and fracture toughness. An alternative way to enhance the ductility of AMCs is to reinforce them with metallic particles such as Ni, Ti, W, Mo, stainless steel, etc. (Yu *et al.*, 2019).

Huang *et al.* (2018) used 5083 Aluminum plates and spherical Ti Powder with a mean size of 23 μm as reinforcements for the fabrication of aluminum composite by FSP technique. The FSP tool used in this research was produced of WC-13 wt percent Co matrix material with an 18 mm diameter shoulder and a 5 mm diameter, 4 mm long, unthreaded cylindrical pin. When flowing

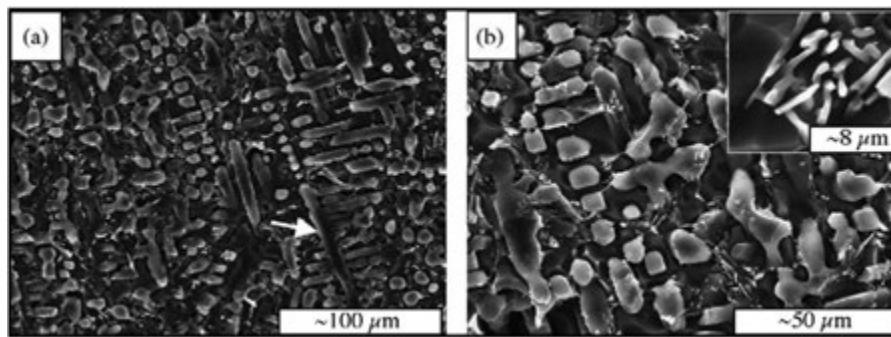


Fig. 14 SEM images at: (a) Lower magnification and (b) higher magnification of Mg_2Si particle in the aluminum matrix. Reproduced from Qin, Q. D., Zhao, Y.G., Cong, P.J., Liang, Y.H., Zhou, W., 2006. Functionally graded $\text{Mg}_2\text{Si}/\text{Al}$ composite produced by an electric arc remelting process. *Journal of Alloys and Compounds* 420 (1–2), 121–125.

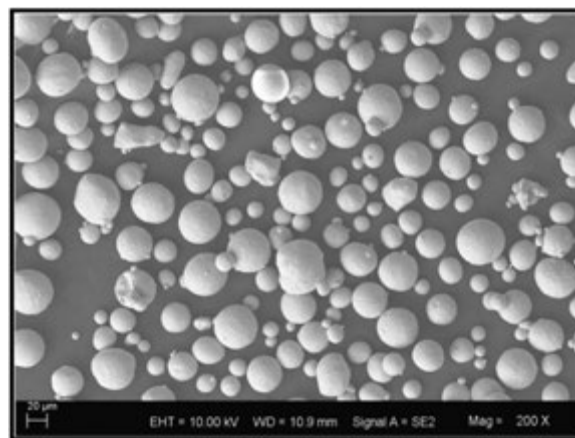


Fig. 15 Morphology of titanium particles. Reproduced from Huang, G., Wu, J., Hou, W., Shen, Y., 2018. Microstructure, mechanical properties and strengthening mechanism of titanium particle reinforced aluminum matrix composites produced by submerged friction stir processing. *Materials Science and Engineering: A* 734, 353–363.

water was fed and balanced, multi-pass was conducted along the same route. Particle distribution, characteristics of the Ti/Al interface was determined by scanning electron microscope (SEM) and shown in Fig. 15. Ti particles within the matrix were homogeneous and demonstrated no particle clustering, as the micrograph shows. Moreover, there was no original spherical particle, and some irregular particles with decreased size were produced. During 5083 Al FSP, ongoing dynamic recrystallization (CDRX) was largely responsible for grain refining. Grain refinement improves strength, while dislocation density reduces.

Selvakumar *et al.* (2017) used FSP to fabricate molybdenum particles (Fig. 16) reinforced Al6082 AMCs. Al6082 rolled aluminum alloy plates of $50 \times 100 \times 10$ mm were used for this investigation. The sheets were machined along the length direction in the center using wire EDM to produce a groove for packing molybdenum particles. The groove length and depth were kept at constant values of 100 and 5.5 mm for all studies. The groove width varied in three steps (0.4, 0.8, and 1.2 mm) so the reinforcement volume fraction will have four levels (0, 6, 12, and 18 vol%). The Mo particles having spherical forms were used for this research. The process parameters used were 1600 rpm tool rotational speed, 60 mm traverse speed and one pass. Machined specimens for microstructural characterization were polished using conventional metallographic procedures and etched. The FSP processed composite FESEM micrographs showed that Mo particles are spread throughout the matrix, indicating that the composite is successfully developed. Mo particles distribution can be considered relatively homogeneous.

Huang *et al.* (2016) used FSP to fabricate Al1060 AMCs reinforced with tungsten (W) particles. Commercially available 1060-H14 pure aluminum alloy was cut into $120 \times 60 \times 5$ mm rectangular sheets. Commercially available tungsten (W) powder was used in this study (99.9% pure and 1–5 mm average particle size). FSP process was carried out using a numerically controlled friction milling machine. Fig. 17 shows the FESEM micrographs of the tungsten powder. Multi-pass FSP reduces W cluster size and facilitates W particle distribution leading to more plastic deformation and rigorous blending related by accumulated plastic strain and continued thermal exposure. FSPed composite strength and ductility were enhanced as FSP passes increase. The increase in tensile strength and ductility of the FSP composite attained after 5 passes and was approximately 126 MPa and 24.73% respectively.

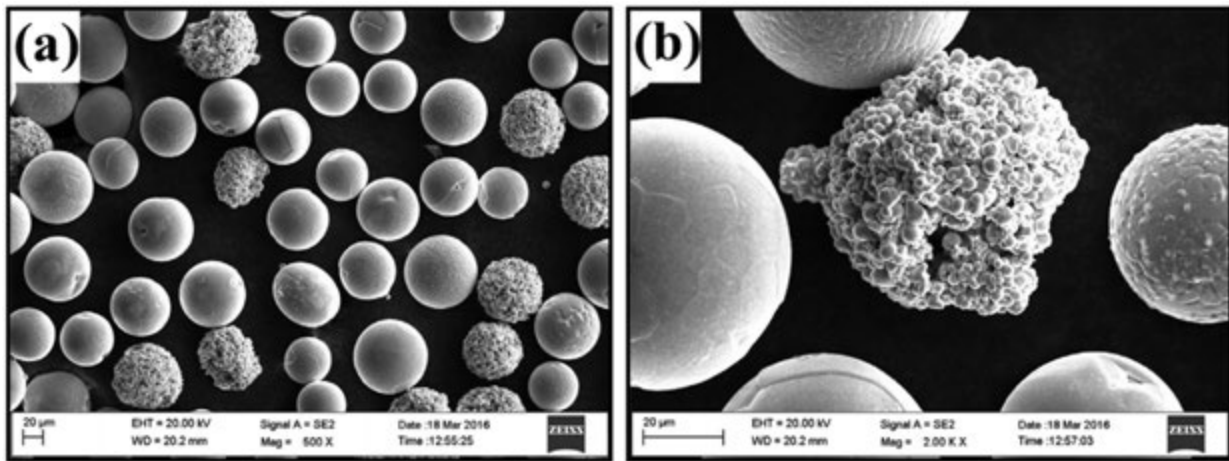


Fig. 16 FESEM micrographs of Mo particles at magnification: (a) 500x and (b) 2000x. Reproduced from Selvakumar, S., Dinaharan, I., Palanivel, R., Babu, B.G., 2017. Characterization of molybdenum particles reinforced Al6082 aluminum matrix composites with improved ductility produced using friction stir processing. *Materials Characterization* 125, 13–22.

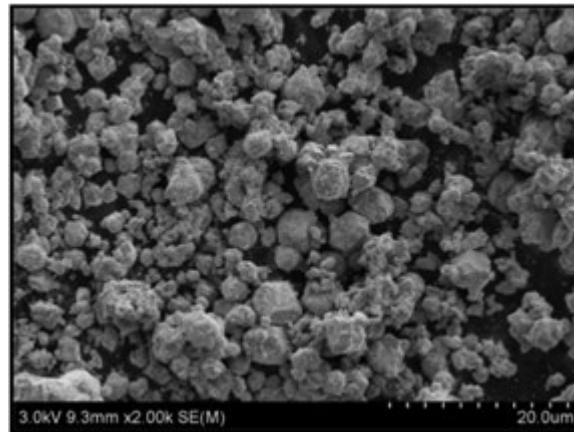


Fig. 17 SEM micrograph of tungsten powder. Reproduced from Huang, G., Shen, Y., Guo, R., Guan, W., 2016. Fabrication of tungsten particles reinforced aluminum matrix composites using multi-pass friction stir processing: Evaluation of microstructural, mechanical and electrical behavior. *Materials Science and Engineering: A* 674, 504–513.

Solid Lubricant Particles

Solid lubricants are needed for lubrication under extreme circumstances where tribological contact bearing surfaces still need to be efficiently separated. Friction leads to the loss of large amounts of mechanical energy, while wear is a significant cause of machine parts failure. A solid lubricant is often described as any solid material that lowers contact surfaces friction and/or wear of contact surface in relative motion. Under very severe circumstances such as elevated temperature, heavy load, ultra-low temperature, ultra-high vacuum, strong oxidation, extreme radiation, etc., solid lubrication can be implemented. Graphite and molybdenum disulfide are commonly used solid lubricants. Besides these two solid lubricants, the other metals used as intrinsic lubricants are metal halides and sulfides (Furlan *et al.*, 2018).

Partheeban *et al.* (2015) fabricated Aluminum 6061 alloy reinforced with 10 wt% of TiB_2 composite and Al6061–10 TiB_2 –1Gr and Al6061–10 TiB_2 –2Gr hybrid composite using powder–metallurgy (P/M) technique. The Al and the reinforcing ingredient of the received TiB_2 powder has a particle size of 30–50 and 1–10 μm , and the size of the graphite particle varies from 25 to 50 μm . The graphite powder used for the fabrication of the AMCs is shown in Fig. 18(a). The microhardness of the manufactured composite Al6061–10 TiB_2 –2Gr increases in addition to the nano-Gr percentage weight increase. There was an improvement in the tensile strength and elongation with the addition of TiB_2 and nano-Gr. But the ductility of a hybrid composite was found to be slightly lower than that of the Al6061 alloy.

Latief and Sherif (2012) used aluminum powder with 99.0% purity and xfoliated graphite nanoplatelets (xGnp) particles to fabricate the AMCs, using powder metallurgy route. The Al powder and received xGnp particles had a particle size of 20 and 7.5 μm .

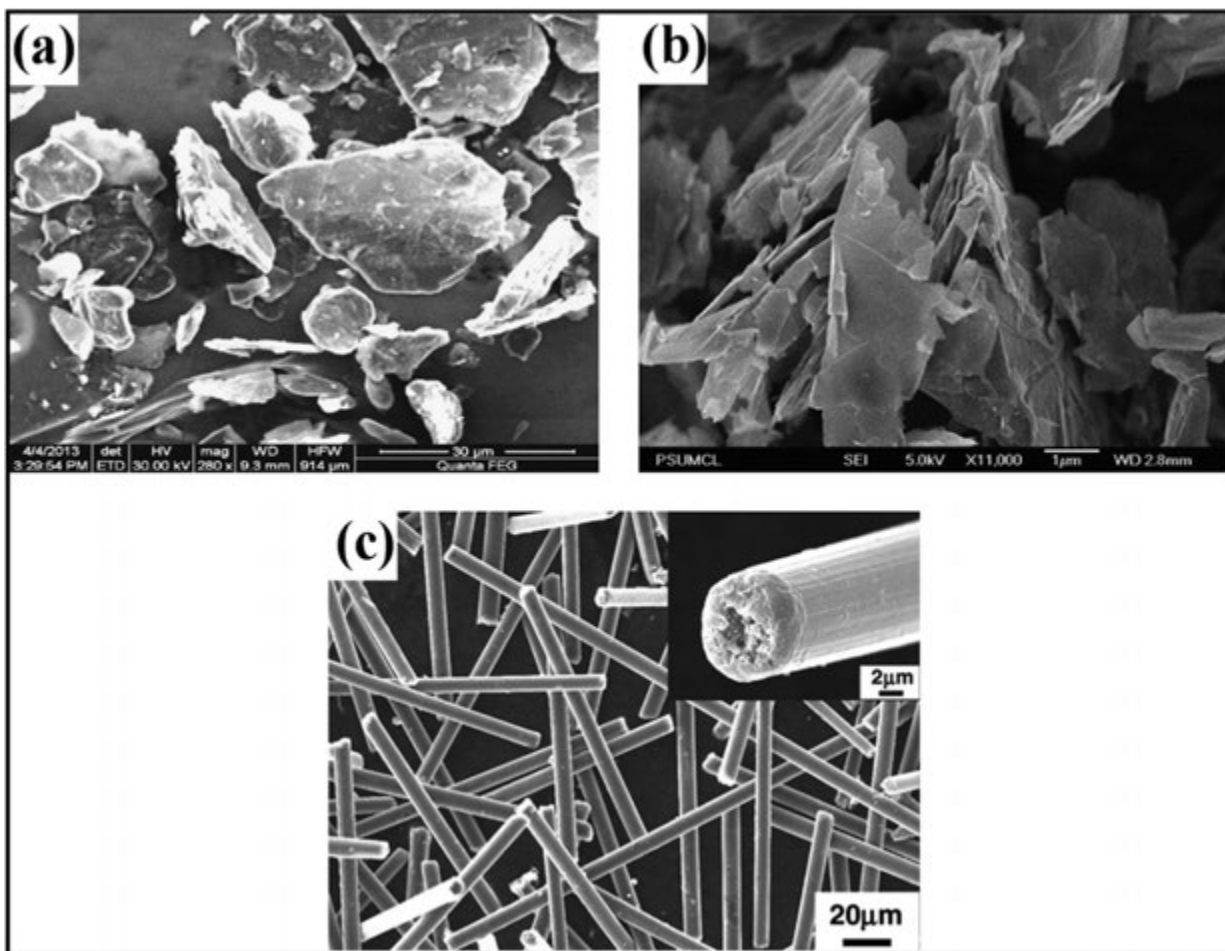


Fig. 18 SEM micrograph of: (a) Graphite powder, (b) graphite nanoplatelets and (c) Ti-coated graphite fibers. Reproduced from (a) Partheeban, C. A., Rajendran, M., Vettivel, S.C., Suresh, S., Moorthi, N.S.V., 2015. Mechanical behavior and failure analysis using online acoustic emission on nano-graphite reinforced Al6061–10TiB₂ hybrid composite using powder metallurgy. *Materials Science and Engineering: A* 632, 1–13; (b) Latief, F.H., Sherif, E.S.M., 2012. Effects of sintering temperature and graphite addition on the mechanical properties of aluminum. *Journal of Industrial and Engineering Chemistry* 18 (6), 2129–2134; (c) Zhang, H.M., He, X.B., Qu, X.H., Liu, Q., Shen, X.Y., 2013. Microstructure and thermal properties of copper matrix composites reinforced with titanium-coated graphite fibers. *Rare Metals* 32 (1), 75–80.

The xGnps are shown in [Fig. 18\(b\)](#). The aluminum powder and xGnp particles were mixed in a disperser machine at a speed of 2000 rpm for 60 min, to obtain a homogenous mixture. The mixture is then green compacted at a pressure of 500 MPa for 5 min to produce a disc-shaped specimen and sintered at varying temperatures. The compressive strength and hardness of the different aluminum alloys increased with increasing the amount of xGnp particles and high sintering temperatures. This effect was found to decrease the relative density of Al–xGnp alloys as a result of shrinkage during the sintering process.

[Zhang et al. \(2013\)](#) used the milled form of mesophase pitch-based graphite fibers. The graphite powder is coated with titanium through chemical vapor deposition technique as shown in [Fig. 18\(c\)](#). The copper and titanium coated graphite powder was mixed, hot pressed and sintered. The Ti-coating reacted with the graphite and formed continuous and uniform TiC layer during the sintering process. This TiC layer established a good metallurgical bonding between the fiber and Cu matrix, which enhances thermal conductivity and reduces CTE of the composites effectively.

[Senthil Kumar et al. \(2016\)](#) prepared tin–copper composite containing MoS₂ to evaluate the tribological behavior through powder metallurgy route. The MoS₂ particles ([Fig. 19](#)) were added to the copper matrix at varying weight percentages (0, 5 and 10 wt%). The fabricated composite was characterized for tribological properties using a pin-on-disc machine. The extruded composites exhibited a lower coefficient of friction (COF) compared to the sintered composite. This is due to the reinforcement of MoS₂ particles as solid reinforcement to the copper composite, which reduces the COF.

[Chi et al. \(2015\)](#) fabricated (TiB₂ + h-BN)/2024Al composites by pressure infiltration technique. The fabricated composite was tested using a pin-on-disc wear tester at room temperature. The addition of h-BN ([Fig. 20](#)) and TiB₂ particles were uniformly dispersed in the 2024Al matrix. The addition of h-BN particles to 2024Al composite acts as a lubricant to enhance the tribological behavior considerably at lower sliding speeds and load conditions. This attributed to the existence of H₃BO₃ and h-BN particles in the fabricated composite.

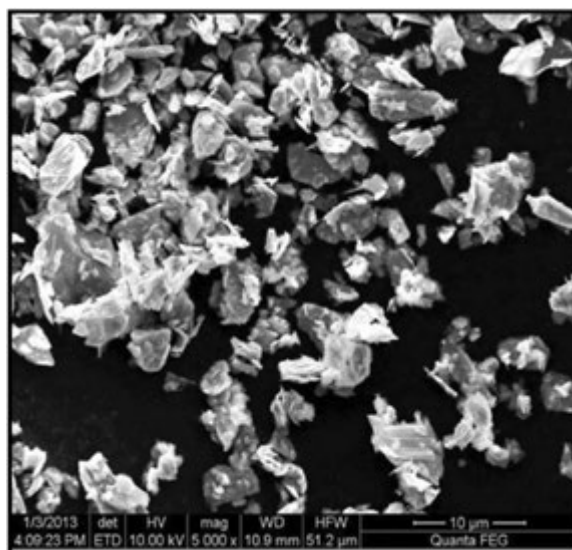


Fig. 19 SEM micrographs of MoS₂ particles. Reproduced from Senthil Kumar, P., Manisekar, K., Vettivel, S.C., 2016. Effect of extrusion on the microstructure and tribological behavior of copper–tin composites containing MoS₂. *Tribology Transactions* 59 (6), 1016–1030.

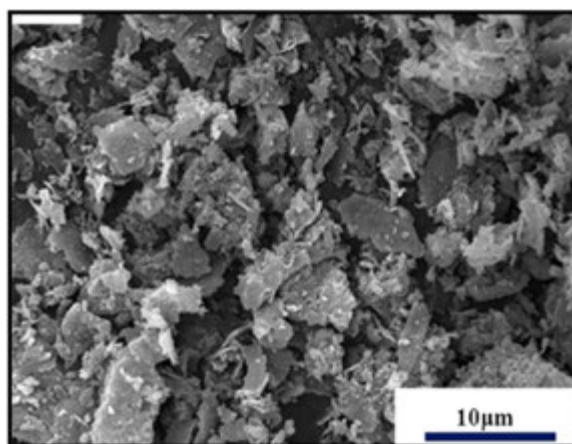


Fig. 20 SEM image of h-BN particles. Reproduced from Chi, H., Jiang, L., Chen, G. *et al.*, 2015. Dry sliding friction and wear behavior of (TiB₂ + h-BN)/2024Al composites. *Materials & Design* 87, 960–968.

Carbonaceous Materials

Carbon is likely mankind's most incredible component. Over the past few years, carbonaceous nanomaterials including carbon nanotubes (CNTs) and graphene have appeared as a significant class of reinforcing nanofillers in polymers, metals and ceramics due to their outstanding mechanical characteristics, good self-lubrication and low density. By customizing the carbon structure, an incredible amount of distinct structures at varying length scale can be acquired. Extensive study has resulted in the synthesis of various types of carbon-based products, including graphene, carbon fiber, fullerenes, and nanotubes (Dinaharan *et al.*, 2017; Bahrami *et al.*, 2016; Kumar and Birru, 2017; Subramaniam *et al.*, 2018; Das *et al.*, 2006). The diverse morphology of various carbon-based products, their accessibility and the flexibility of altering physical characteristics are some of the main factors for gaining greater attention compared to the other components in contemporary material science.

Carbon nanotubes

Due to their remarkable elevated elastic modulus, mechanical strength and exceptional electrical and thermal conductivity, carbonaceous nanomaterials including graphene and carbon nanotubes (CNTs) have appeared as a significant class of new materials for structural engineering in recent years. CNTs are regarded as the most effective reinforcement additives for producing composite materials in combination with their high aspect ratio. Introducing such reinforcements into metal matrices strongly enriches the hardness, tensile strength, elastic modulus, and other mechanical properties. Several other characteristics such as thermal conductivity (TC), thermal expansion coefficient (CTE), friction coefficient, wear resistance,

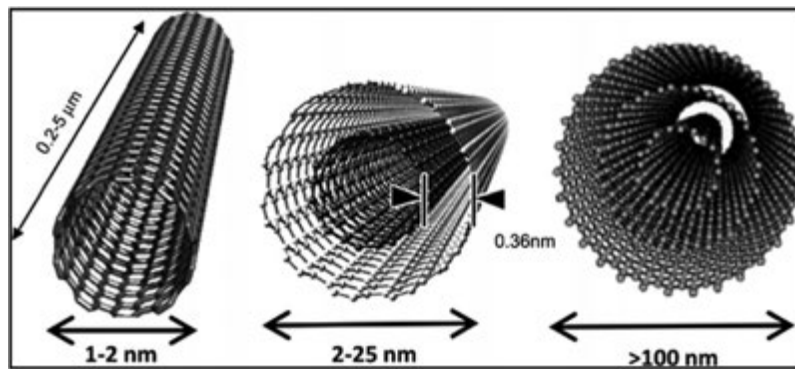


Fig. 21 Schematic of Single-, double-, and multi-walled CNTs. Reproduced from Moghadam, A.D., Omrani, E., Menezes, P.L., Rohatgi, P.K., 2015. Mechanical and tribological properties of self-lubricating metal matrix nanocomposites reinforced by carbon nanotubes (CNTs) and graphene – A review. Composites Part B: Engineering 77, 402–420.

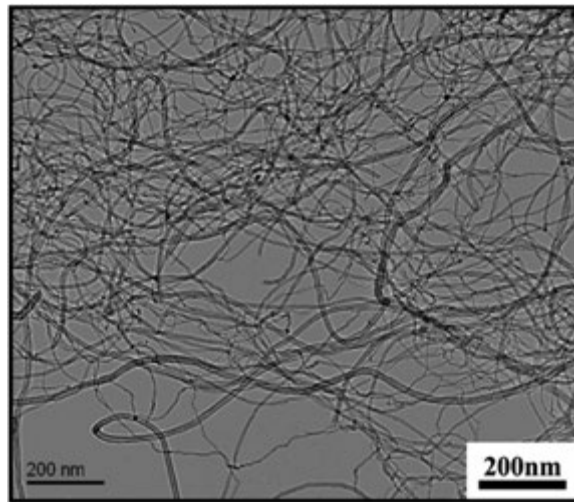


Fig. 22 Morphology of single walled CNTs. Reproduced from Liu, Z.Y., Xiao, B.L., Wang, W.G., Ma, Z.Y., 2013. Developing high-performance aluminum matrix composites with directionally aligned carbon nanotubes by combining friction stir processing and subsequent rolling. Carbon 62, 35–42.

corrosion, and fatigue resistance can also be customized to MMC demands. Several types of nanotubes exist; but they can be divided into two main categories namely, single-walled (SWNT), Double-walled carbon nanotubes (DWCNTs) and multi-walled (MWNT) as shown in Fig. 21. SWCNTs are hollow long cylinders made of one atomic sheet of carbon atoms in a hexagonal or honeycomb crystal structure. DWCNTs are a synthetic combination of single-walled and multi-walled nanotubes, showing medium characteristics of both forms. DWCNTs may develop four distinct possible combinations which are electronic type, inner and outer membranes, either metallic or semiconducting, material (not clear). MWCNTs are elongated and made of sp² carbon hollow tubular nano-objects. The diameter of MWCNTs is 3–30 nm and they can be several micrometers long, but their aspect ratio can differ between 10 and 10 million. A MWCNT's wall thickness is relatively continuous along the axis, making the inner tube to be straight (Moghadam *et al.*, 2015).

Graphene

Liu *et al.* (2013) used CNTs to fabricate 1.5–4.5 vol% carbon nanotube (CNT)-reinforced 2009Al composites by FSP and subsequent rolling processing. The morphology of the used CNT has an outer diameter of 10–20 nm for the fabrication of aluminum composite as shown in Fig. 22. FSP plus subsequent hot rolling was used effectively to produce 1.5–4.5 vol. percent CNT/2009Al composites with uniformly dispersed and spatially aligned CNTs. The CNT–Al interfaces were well attached, retaining the CNT's tube morphology. FSP-rolled CNT/2009Al's YS and UTS values were substantially greater than those of matrix alloy. The FSP-rolled composites with spatially aligned CNTs displayed much greater strength, ductility and modulus values compared to the FSP composites with randomly distributed CNTs.

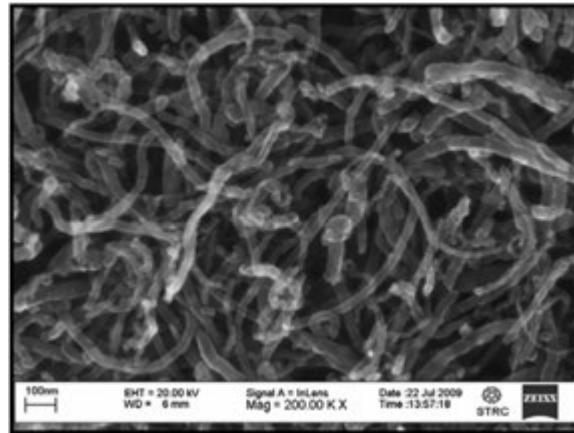


Fig. 23 Morphology of MWCNTs: 30–50 nm in diameter and 10–20 μm in length. Reproduced from Esawi, A.M.K., Morsi, K., Sayed, A., Taher, M., Lanka, S., 2010. Effect of carbon nanotube (CNT) content on the mechanical properties of CNT-reinforced aluminium composites. *Composites Science and Technology* 70 (16), 2237–2241.

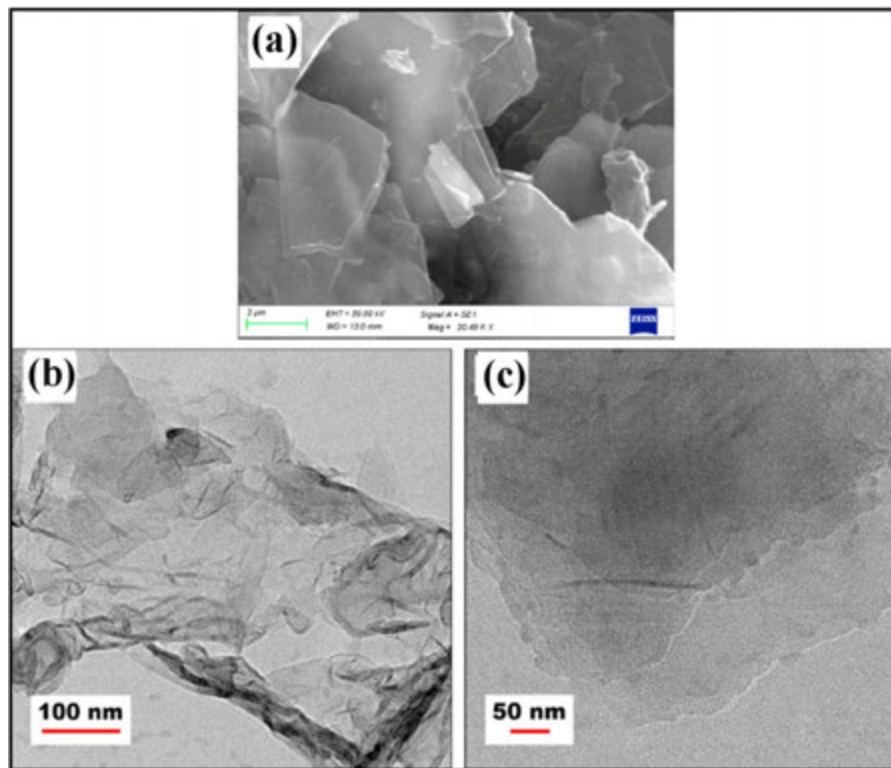


Fig. 24 Morphology of Graphene nanoplatelets (a) SEM, (b) and (c) TEM morphology of graphene nanoplatelets. Reproduced from Sharma, A., Sharma, V.M., Sahoo, B., Pal, S.K., Paul, J., 2019. Effect of multiple micro channel reinforcement filling strategy on Al6061-graphene nanocomposite fabricated through friction stir processing. *Journal of Manufacturing Processes* 37, 53–70.

Esawi *et al.* (2010) used CNTs to fabricate varying weight percentages (0, 1, 2 and 5 wt%) of CNT-reinforced aluminum composite by powder metallurgy route. The morphology of the used CNT has an outer diameter of 30–50 nm and length of 10–20 μm CNTs used for the fabrication of aluminum composite is shown in Fig. 23. The mechanical properties of the fabricated aluminum composite enhanced by up to 50% in tensile strength and 23% in stiffness compared to that of pure aluminum.

Sharma *et al.* (2019) fabricated AA6061 aluminum composite by reinforcing graphene nanoplatelets (GNP) using multi-pass friction stir processing (MPFSP) technique. The GNP of 3–10 layers and size 5–10 nm with 5 μm lateral dimension was used as reinforcement as shown in Fig. 24. EBSD and optical microscopy revealed a higher degree of grain refinement and increased width of the processing zone. SEM study revealed the GNP particles to be homogeneously distributed in the Al matrix. The tensile study

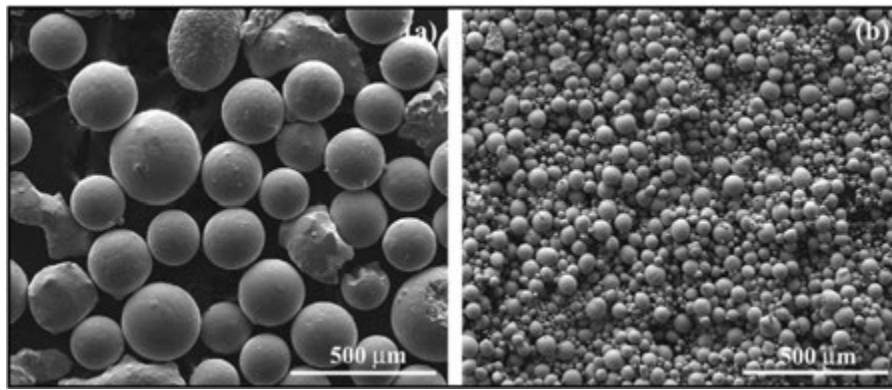


Fig. 25 Morphologies of NiTiP shape memory particle with sizes of (a) 150–178 μm and (b) 2–74 μm . Reproduced from Ni, D.R., Wang, J.J., Zhou, Z.N., Ma, Z.Y., 2014. Fabrication and mechanical properties of bulk NiTiP/Al composites prepared by friction stir processing. *Journal of Alloys and Compounds* 586, 368–374.

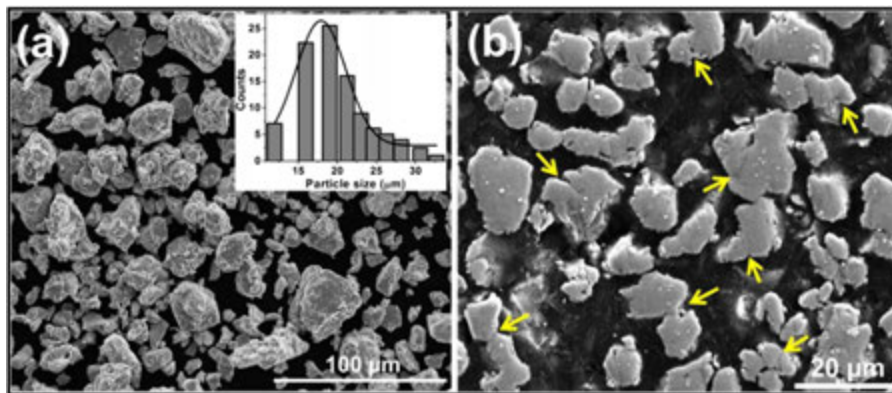


Fig. 26 SEM micrographs of CoCrFeNi high entropy alloy powder: (a) Ultrasonicated loose powder, (b) mounted and metallographically polished powder. Inset in (a) shows the particle size distribution (based on laser particle size analysis). Arrows in (b) show some powder particles that are composed of weakly-bonded sub-particles. Reproduced from Karthik, G.M., Panikar, S., Ram, G.J., Kottada, R.S., 2017. Additive manufacturing of an aluminum matrix composite reinforced with nanocrystalline high-entropy alloy particles. *Materials Science and Engineering: A* 679, 193–203.

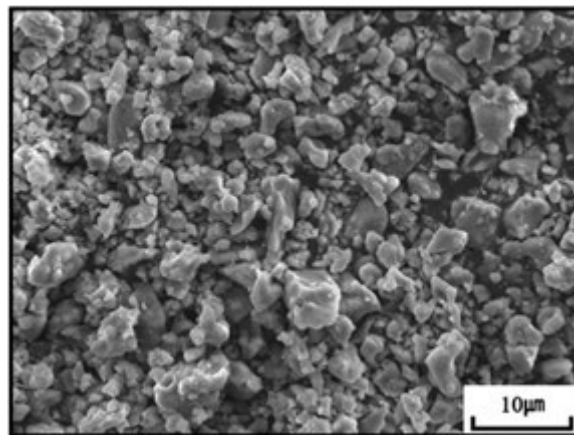


Fig. 27 SEM image of hydroxyapatite powder. Reproduced from Khanra, A.K., Jung, H.C., Hong, K.S., Shin, K.S., 2010. Comparative property study on extruded Mg–HAP and ZM61–HAP composites. *Materials Science and Engineering: A* 527 (23), 6283–6288.

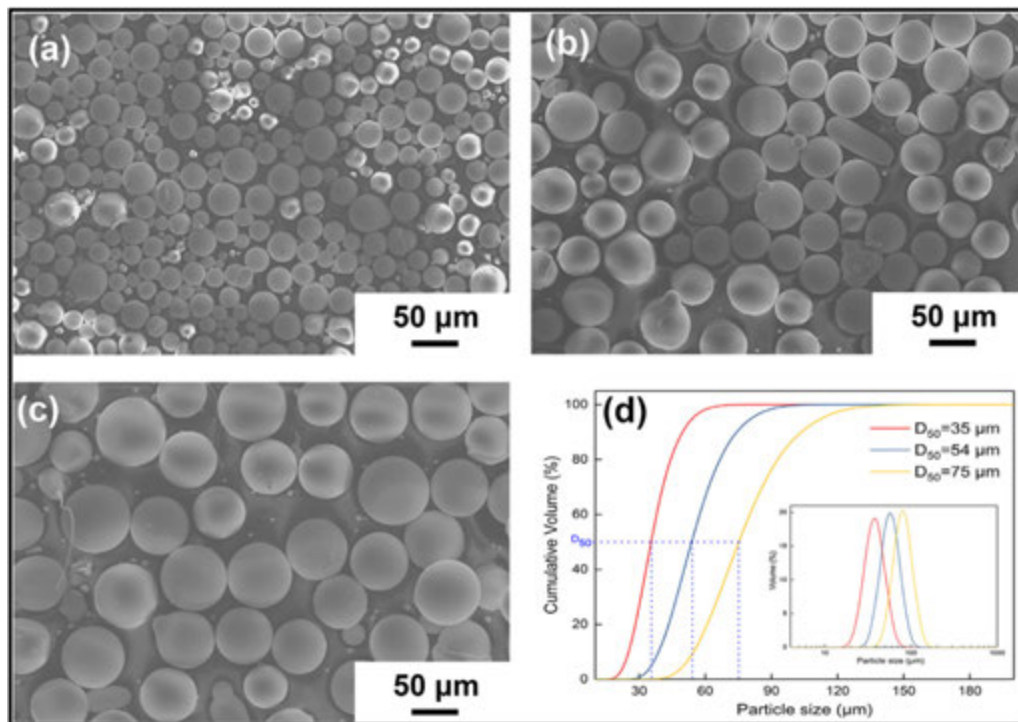


Fig. 28 SEM micrographs of $\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$ metallic glass powders with average size (a) 35 μm , (b) 54 μm and (c) 75 μm ; (d) particle size distributions. Reproduced from He, T., Ertuğrul, O., Ciftci, N., *et al.*, 2019. Effect of particle size ratio on microstructure and mechanical properties of aluminum matrix composites reinforced with $\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$ metallic glass particles. *Materials Science and Engineering: A* 742, 517–525.

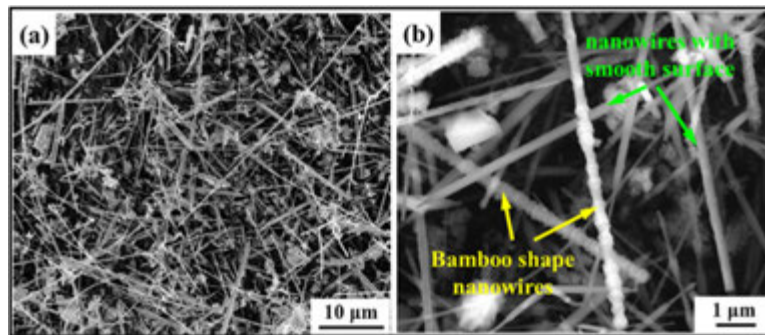


Fig. 29 Representative morphology of SiC nanowires. (a) Morphology, (b) Magnification of nanowires. Reproduced from Dong, R., Yang, W., Wu, P., *et al.*, 2015. Microstructure characterization of SiC nanowires as reinforcements in composites. *Materials Characterization* 103, 37–41.

reveals an increase in UTS by $\sim 28\%$ and an increase in surface nano-hardness by $\sim 84\%$ in the composite fabricated through the MPFSP.

Miscellaneous

Other reinforcement particles used for the fabrication of MMCs are CoCrFeNi high entropy alloy powder, hydroxyapatite particle, glass powders, nano wires or whiskers, etc., These particles reinforced in MMCs were fabricated using various techniques that are explained in detail from various works of literature. Ni *et al.* (2014) fabricated NiTi reinforced AA6061-T65 aluminum composite by FSP. The NiTi powder selected for the FSP has a size range of 0–178 and 2–74 μm as shown in Fig. 25. The FSP fabricated composites show lower tensile strengths and higher elongation than the as-received AA6061-T651, but the strength increased after the aging treatments without any interfacial products being detected.

Karthik *et al.* (2017) fabricated aluminum composite using AA5083 matrix reinforced with CoCrFeNi high-entropy alloy particles successfully by friction deposition in multiple layers. The CoCrFeNi high-entropy alloy particles are shown in Fig. 26. The

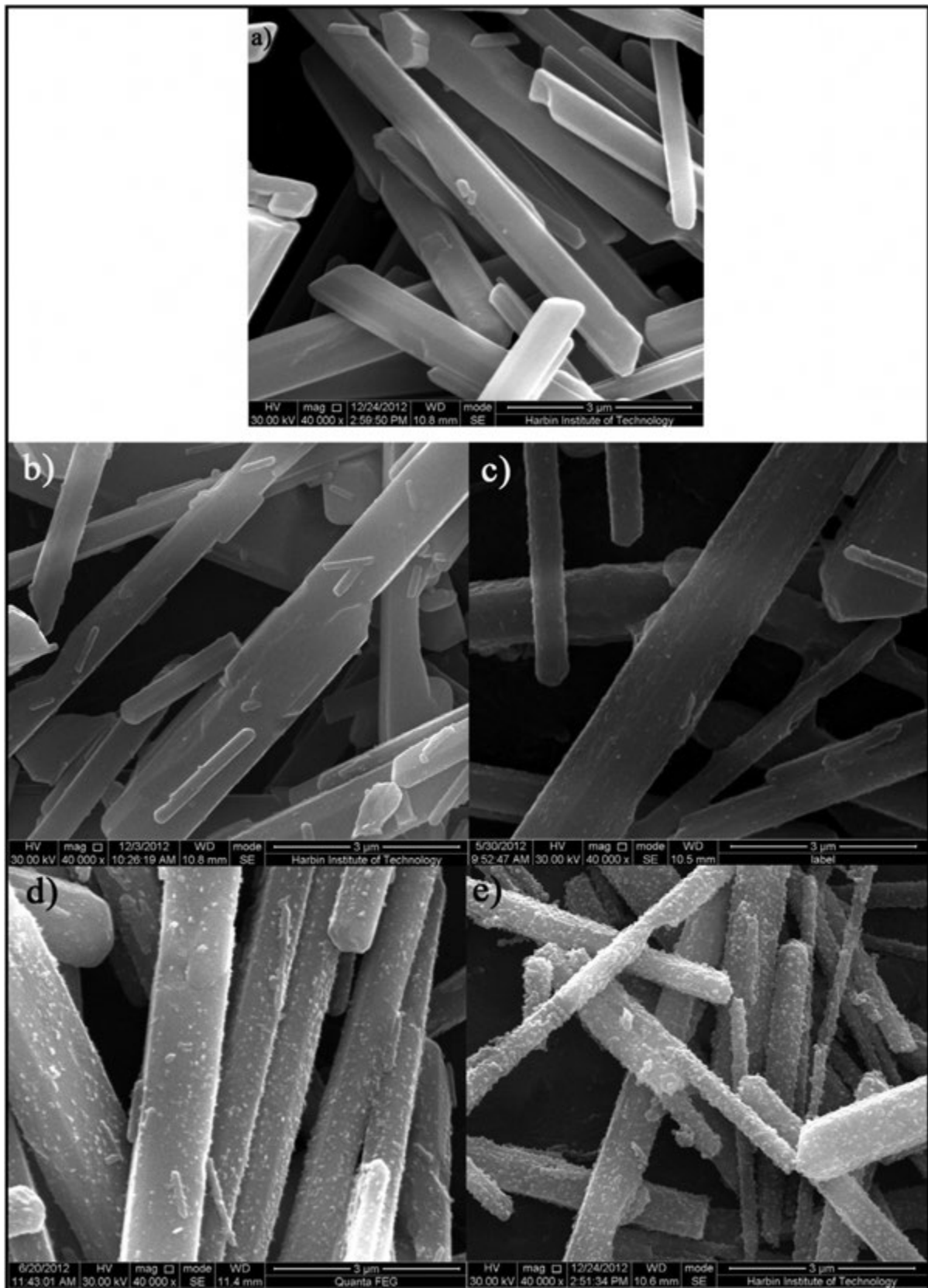


Fig. 30 Surface morphologies of the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers without and with Al_2O_3 coatings prepared at the different hydrothermal temperature: (a) Uncoated whiskers, (b) 140°C , (c) 160°C , (d) 180°C , (e) 200°C . Reproduced from Tang, S.W., Liu, C., Yu, Y.C., Hu, J., Kong, L.C., 2015. The microstructure and tensile properties of Al_2O_3 -coated $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whisker reinforced AA2024 aluminum composite. *Materials Chemistry and Physics* 149, 282–287.

high-entropy alloy particles were ball milled for 15 h and deposited over the AA5683 matrix by using friction stir welding machine at a load of 200 kN, by employing a consumable rod of AA5083 of the same material as the substrate. The fabricated composite exhibited higher tensile and compressive strength than the AA5083 matrix alloy.

Khanra *et al.* (2010) in their work, fabricated hydroxyapatite (HAP) particles reinforced Mg-HAP and ZM61-HAP composite through liquid metallurgy route. The morphology of HAP powder is shown in Fig. 27. After solidification process, the ingots were subjected to homogenizing treatment for 12 h at 400°C and extruded at a temperature of 320°C. The presence of HAP particles in the composite reduced the grain size during the extrusion process. The tensile strength and hardness values were higher in ZM61-HAP composite than the Mg-HAP composite.

He *et al.* (2019) fabricated aluminum matrix composites reinforced with $Zr_{48}Cu_{36}Ag_8Al_8$ metallic glass particles by using powder metallurgy route. The aluminum powder with a mean size of 13 μm and $Zr_{48}Cu_{36}Ag_8Al_8$ (at%) metallic glass particle with a mean size of 35, 54, and 75 μm was selected for fabricating the aluminum composite as shown in Fig. 28. The compressive and tensile yield strength of the composites are not sensitive to the particle size ratio change, whereas the ultimate tensile strength and the ductility are significantly reduced with decreasing particle size ratio. This behavior is accompanied by the change of the fracture mode.

Dong *et al.* (2015) used silicon carbide nanowire (SiCnw) as reinforcement to fabricate AA6061/SiCnw through pressure infiltration process. The SiCnw used for the reinforcement was cylindrical type with smooth surface and bamboo shape as shown in Fig. 29. The author successfully fabricated the aluminum composite and examined using SEM and TEM, which confirmed the presence of the SiCnw that consisted of a large number of small fragments that are formed by hybrid 3C-SiC and 2H-SiC structures.

Tang *et al.* (2015) fabricated Al_2O_3 -coated $Al_{18}B_4O_{33}$ whiskers reinforced AA2024 matrix composites by squeeze casting process. Fig. 30 shows the surface morphologies of ABO_w without and with Al_2O_3 coating prepared at the different hydrothermal temperatures. The coating on Al_2O_3 particles effectively reduces the interfacial reaction. The coating on Al_2O_3 enhances the tensile property of the composite and the effect of age hardening of the fabricated aluminum composite.

Summary and Future Outlook

In this article, the various matrix and reinforcement materials used for the production of MMC were presented. The various factors to be considered for the selection of matrix and reinforcement during the fabrication process were presented in detail.

Various conventional methods and specific patented methods have been used to fabricate AMCs reinforced with different types of ceramic particles which include but not limited to powder metallurgy, mechanical alloying, stir casting, squeeze casting, and spray deposition. The major drawback in powder metallurgy (PM) route is the high cost of the metal powder, tooling and equipment. The components produced by PM can also have lower ductility and strength. A major drawback in stir casting is the wettability between the molten aluminum matrix and the ceramic particle. Various methods were attempted by researchers to improve wettability which includes adding wettability agents and fluxes, preheating the ceramic particle and coating the ceramic particle. Those techniques increased the cost of fabrication. Traditionally, the most in demand matrix materials are aluminum, magnesium, copper and titanium due to the combination of properties such as low density, high ductility, corrosion resistance and superior strength-to-weight ratio, compared to steel.

Researchers explored the possibilities of carbon nanotubes, hydroxyapatite, CoCrFeNi high-entropy alloy particles and glass particles as reinforcement for the fabrication of MMCs. Among the various reinforcements discussed, the carbonous materials are found to have many favorable attributes such as high thermal conductivity, low coefficient of thermal expansion, high damping capacity and good self-lubricating property. These favorable properties can be achieved only if the reinforcements are dispersed uniformly and not agglomerated in the matrix.

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Composite Materials Production for Automobile Applications

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Introduction

Automotive manufacturing industries face many challenges including enhancing energy efficiency, reducing exhaust emissions, increasing safety, and reducing the manufacture cost. Many of the composite production scientists, Automotive engineers work together to address these kind of challenges to develop and leading solutions at highest standards (Frosch and Gallopoulos, 1989). The main goal of the automotive industry is to reduce the vehicle mass or develop a new design for the vehicles, to deliver the optimum solution and robust product portfolio which offer the lightweight, cost-effective, multifunctional-material technology. The composite materials future market gain presents promising opportunities in automotive, aerospace, consumer goods, medical, infrastructure, and marine industries. Aerospace and automotive industries are the major drivers in increasing use of composite materials and still there a growing demand of composite preforms manufacture (Weinert *et al.*, 2008). This enables the manufacture of complex shaped structures and specifically shorten the part cycle time.

A strong encouragement to apply composites to automotive sector comes essentially from guidelines aimed at drastic reduction of CO₂ emission per unit distance. Fig. 1 represents countries worldwide implementing the regulations to reduce CO₂ output per km. According to the EURO 6 regulations, high tax will be collected to the vehicles exceeding the 95 g km⁻¹ of CO₂ and because of this regulations automobile manufacturing companies have been undertaking the research and development towards new technologies. Overall weight reduction of automobile vehicles, especially structural weight is very influential in reducing CO₂ emissions (Lovins and Lovins, 1991). Hence, efforts towards to pursue the light weight automotive vehicles become a significant challenge for the manufactures globally.

Adoption of advanced composites in the automotive sector has been complicated due to high costs of production and further, competition with other aluminum based light weight materials. In addition, composite production cycle is low, and there are no defined end-of-life for the particular materials. Further, composite materials are difficult to recycle or reshaped after the accident. Out of these hurdles, car manufactures are adopting hybrid composite materials increasingly with the goal of reducing the weight, there by downsizing the engine without sacrificing the efficiency (Fuchs *et al.*, 2008). This making the implementation of new policies and regulations for the car manufacturing companies to approve the composite materials adoption.

The global Automotive Composite Market (GACM) is basically categorized based on the material (glass fiber, carbon fiber composite, natural fiber, aramid fiber and others), type of resin (thermoset and thermoplastic). Out of all, continuous fiber-reinforced thermoplastics composites (CFRTP) gained key interest and immediate adoption to the automotive community for it production and parts applications (Goh *et al.*, 2018). Most of the such composites materials depend on the fiber location and integrations which enables the enhancing and direct functioning of the composites. Many of the automotive composite industries require combination of process and technology breakthroughs in manufacturing composite. Currently, thermoforming method was the widely adopted technology due to its shorter cycle time and usage of existing equipment's without much up gradation. Further, thermoforming and stamping methods can easily automate.

The primary applications of the composite are limited now for only structural areas including vehicle body and other small components and still have lot of scope for expanding in this area in the automobile sector. But, the design of composite for the automobile applications currently looking for durability and the energy absorption capabilities. Most of the composites now clear with these fundamental properties in terms of high energy absorption before failure but the other major challenge is translating same capabilities to complex shaped structures with high defined loads (Beardmore and Johnson, 1986). Other important requirement functional requirement for the composites are vibration noise and harness (NVH). These factor further depends on the stiffness of the composites and very far to compete with steel and other conventional structural materials.

The need of computer simulations to manufacture the composite materials become key factor to obtain a desired part quality, to optimize the production time and for the economical production. Most of the manufacturing techniques ended with some of the defects and computer simulation is must to avoid the defects like, variation in the thickness, wrinkling, ununiformed distribution of resin and fiber waviness. Simulation also helps in to determine the various processing conditions like temperature, forming speed and geometry of the reinforcement, etc., to optimize the structure and the quality. Further, the failure of the fiber in microscopic level can't be observed at macroscopic range and macroscopic wrinkling can't be observed at microscopic range (Frosch and Gallopoulos, 1989; Lovins and Lovins, 1991; Tong *et al.*, 2002). So this needs different simulations in various scale range to study the behaviors and various characteristics of the reinforcement and formability characteristics of a complex geometrical shapes.

This article summarizes the market trend, advanced reinforce materials, production techniques and adaption of advanced composites to automotive applications. Further, this work enables the new research site and studies in order to investigate the adoption of potential use of composites in various automotive structural components. The important to note that the most of



Fig. 1 Trends of environmental awareness globally. Reproduced from Girod, B., van Vuuren, D.P., de Vries, B., 2013. Transportation Research Part A: Policy and Practice 50, 183–197.

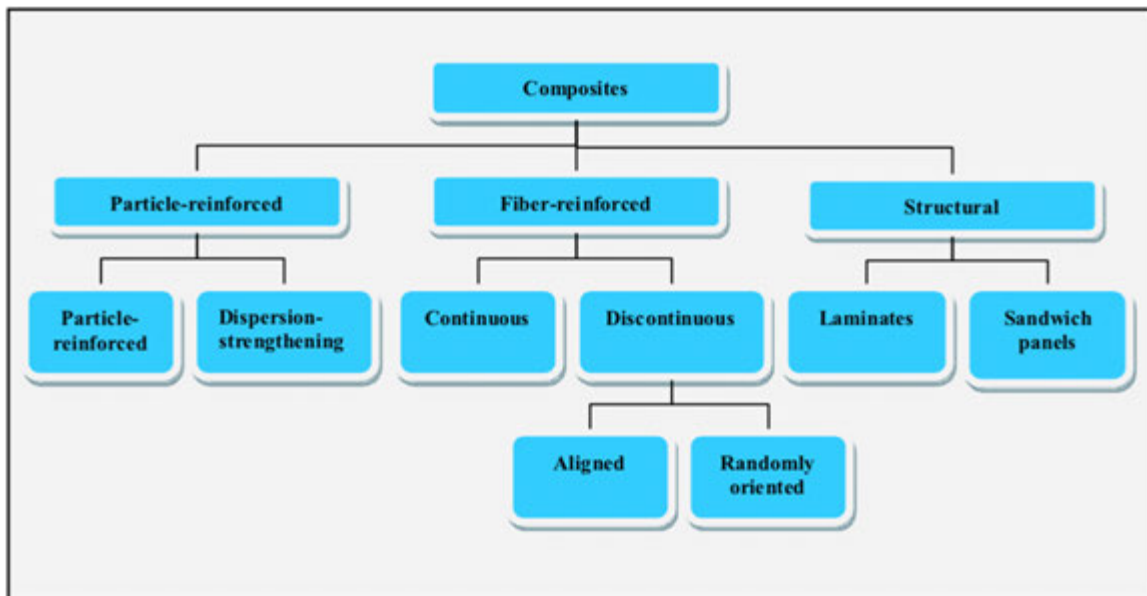


Fig. 2 Classification of composite materials. Reproduced from Callister Jr., W.D., 2007. Material Science and Engineering: An Introduction. seventh ed. New York: John Wiley & Sons.

studies were made on enhancing the various mechanical properties of the automotive parts including to provide the better ecological and economical solutions.

Composite Materials Classification

Composite materials basically made up of two or more physically or/and chemically distinct materials and these are separated by matrix phase and reinforcement phase. Both the phases place a big role on enhancing the properties composites in terms of better load bearing capacity of both and it can be classified depending upon the types of matrix and reinforcement phases as shown in Fig. 2.

The matrix also categorized into metal matrix, ceramic matrix, and polymer matrix and grouped into Metal Matrix Composites (MMC), Ceramic matrix composites (CMC) and Polymer Matrix Composites (PMC) as shown in Fig. 3. In all the categories, the main function of the matrix in the composite structure is to bind the reinforcement together and transfer the load (Callister, 2007). Besides, it offers the rigidity and act as reinforcement protector from the chemical and other mechanical damages. Reinforcement is also an important constituent in any of the composite categories and it carries

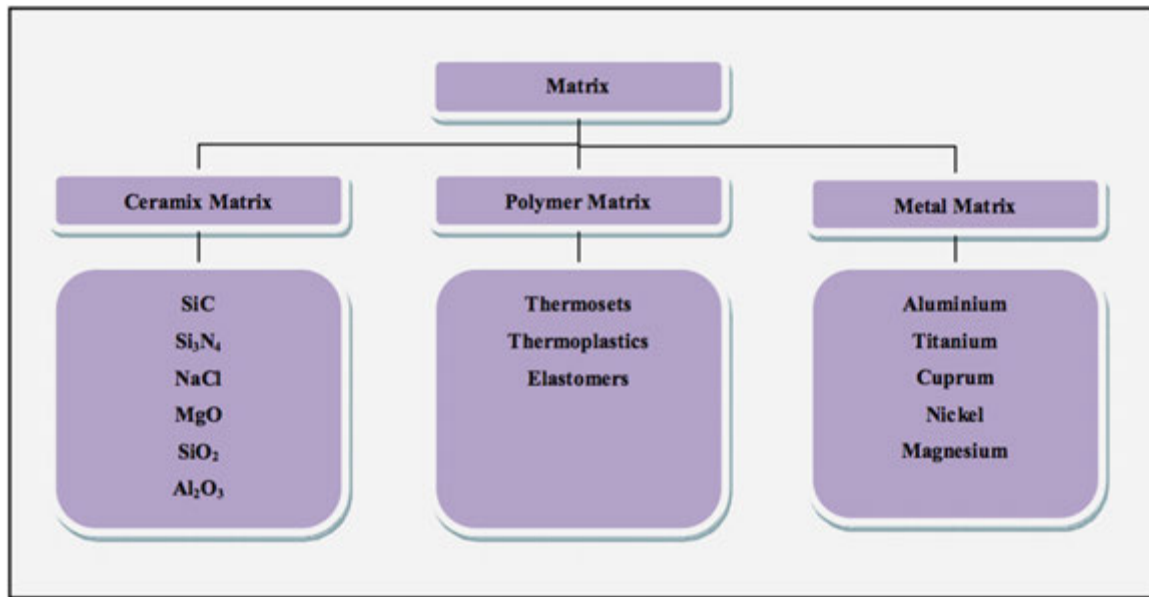


Fig. 3 Types of matrix used in composites. Reproduced from Matthews, F.L., Rawlings, R.D., 1999. Composite Materials: Engineering Science. seventh ed. Boca Raton: CRC Press.

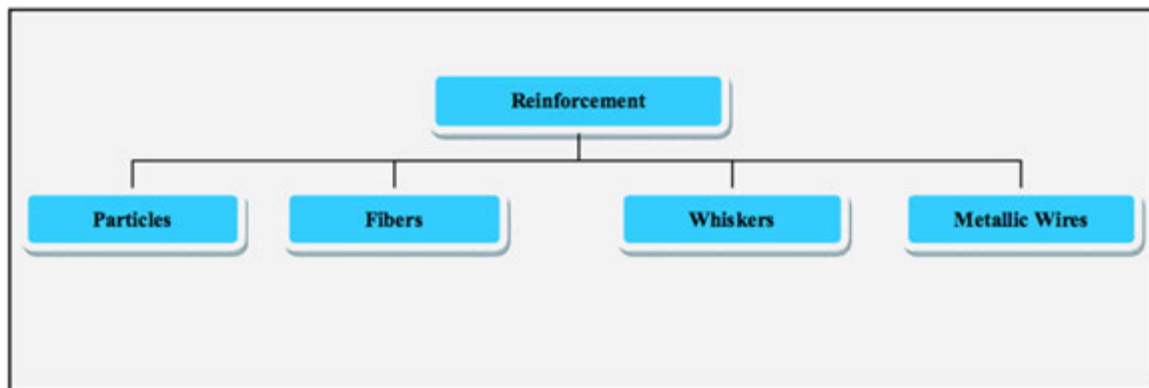


Fig. 4 Types of reinforcement used in composites. Reproduced from Callister Jr., W.D., 2007. Material Science and Engineering: An Introduction. seventh ed. New York: John Wiley & Sons.

80%–90% of the load which to it. It also acts as barrier to the cracks propagation and enhances the life of the composites. Reinforcement can be categorized into fibers, particles, whiskers, and metallic wires as shown in Fig. 4. Reinforcements in the composites will provide the strength to the composites and must be stronger and stiffer than the matrix material in the composite. These materials also help in changing the actual failure mechanism of the composites and this need matrix should have minimum brittleness.

Polymer Matrix Composites (PMC)

PMCs are most commonly used composites compared to other types of campsites particularly in automobile sector due its tunes strength, light weight, and stiffness. Also, its offers ease of fabrication, better reinforcing capabilities to achieve desired properties. Processing of PMCs require only minimum temperature and pressure, which can be produced very rapidly. Basically PMCs reinforces with carbon, aramid, and glass fibers however these days' synthetic fibers got high attraction in this field to lower the price and sustainable resources.

Laminates panels and sandwich panels are the most common structure used to fabricate the PMCs and both the structure are important in the composites to produce desired properties of the composites. Further, geometrical arrangements of the laminates and the fire are place a crucial role to create the strengthened composites materials for critical automobile applications. Laminate

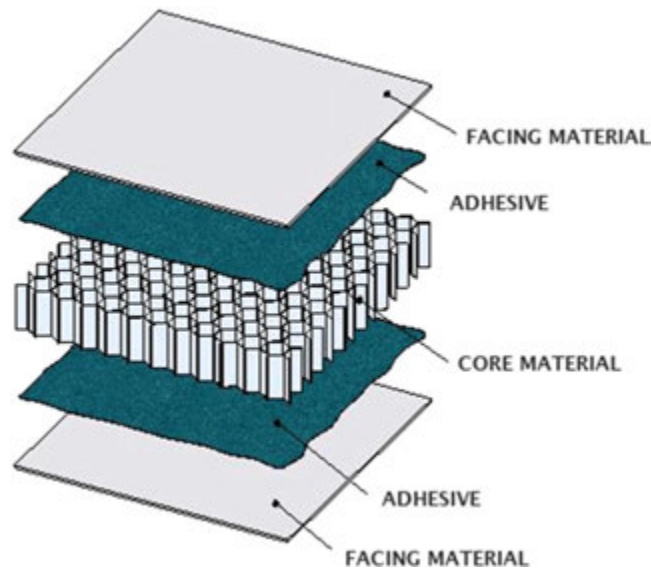


Fig. 5 Schematics of PMCs laminate panel and sandwich panels. Reproduced from Callister Jr., W.D., 2007. Material Science and Engineering: An Introduction. seventh ed. New York: John Wiley & Sons.

panels possess highest strength which are basically plate type of shells reinforced with layered materials in different orientations and stacked layer by layer (Fig. 5). This kind of structure are specifically used in automobile applications. Basically, Sandwich panels exist in two outer face sheets and a core in between. This specific structure and combination offers the greater strength and stiffness and its light weight when used in composite fabrications. To build sandwich composites, laminated composites can be used as face sheets or sometimes, titanium, steel, or aluminum sheets are also used as face sheet. The core of this kind of composites filled with low density synthetic rubber, balsa wood, or inorganic cement (Callister, 2007; Matthews and Rawlings, 1999). This kind of a composites are used on sporting, automobile, and aerospace industries. The importance of the polymer is shown in Fig. 6.

Composite Materials Production

Hot Drape Forming (HDF)

The process of preforming prepreg plies on the pattern and mold is termed as Hot Drape Form (HDF). HDF is basically a thermoforming process which involves stacking of prepegs on the mold in a single step. The suitable mobile structure placed on the worktop, which includes infrared lamps for heating and curing, vacuum system, and elastic membrane were used to forming process. The cut and stratified prepegs are placed on the polished mold and subjected to vacuum-heat by using elastic membrane. This process gives the final shape and accuracy to the preform to the plies. Thus, obtained preforms are from the HDF machine are cured in an autoclave (Fig. 7). The HDF process is a mass production technique where, process time is reduced there by stratifying of many plies in defines plane will be faster. In addition, the process is repeatable and more reliable. Currently, this technology is accepted and using in various manufacturing industries. Further, careful planning, computer simulations, and sophisticated tools are required to proper implementation of this process to avoid the damaged parts (Ott, 1994; Sjölander *et al.*, 2016).

The HDF technique basically reduces the time required for the layer by layer lay-up on to the three dimensional pattern. But, the process is profound to complexity of component dimensions and complexity. Further, achieving of high forming efficiency is difficult and it may lead to wrinkling or fiber buckling around the geometric feature (Fig. 8) (Dodwell *et al.*, 2014). However, during the process heat is applied to reduce the viscosity of the resin to prevent surface ply slippage and this may cause the high interplay shear stress. Further, when the shear stress exceeds the during deformation can cause compressive stresses on the ply lead to fiber buckling. These defects are influenced by forming speed, temperature and may be depending upon the length of deformation (l_{crit}) and wrinkling defect may have generated if this length ($> l_{crit}$) is too long to countenance the slippage (Sjölander *et al.*, 2016; Dodwell *et al.*, 2014). Thus, HDF process is suitable for manufacturing of smaller and thin sections components.

Composite Thermo Stamping (CTS)

Composite stamping process is the one of the most promising economical and high performance composite components for the automotive industry. The stamping process is very similar to conventional metal stamping process and one of the key benefit of this method is short cycle time manufacture of continuous thermoplastic composites for the light weight automotive parts. The

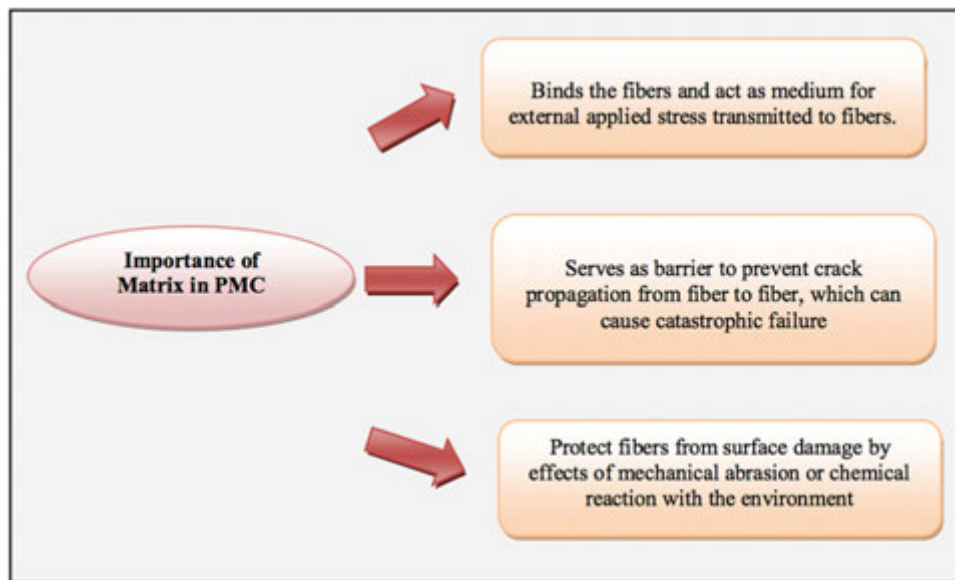


Fig. 6 Importance of polymer matrix in PMC.

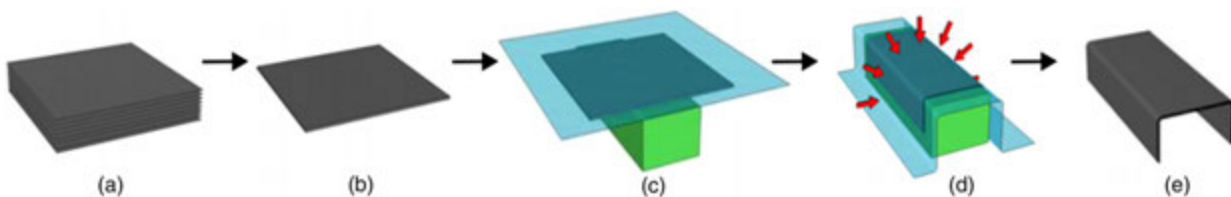


Fig. 7 HDF process (a) prepeg stock (b) Uncured Laminate (c) Place a laminate and diaphragm on top of the pattern (d) Shape with external heat (e) Shaped laminate on top of the pattern. Reproduced from Sjölander, J., Hallander, P., Åkermo, M., 2016. Composites Part A: Applied Science and Manufacturing 81, 41–51.

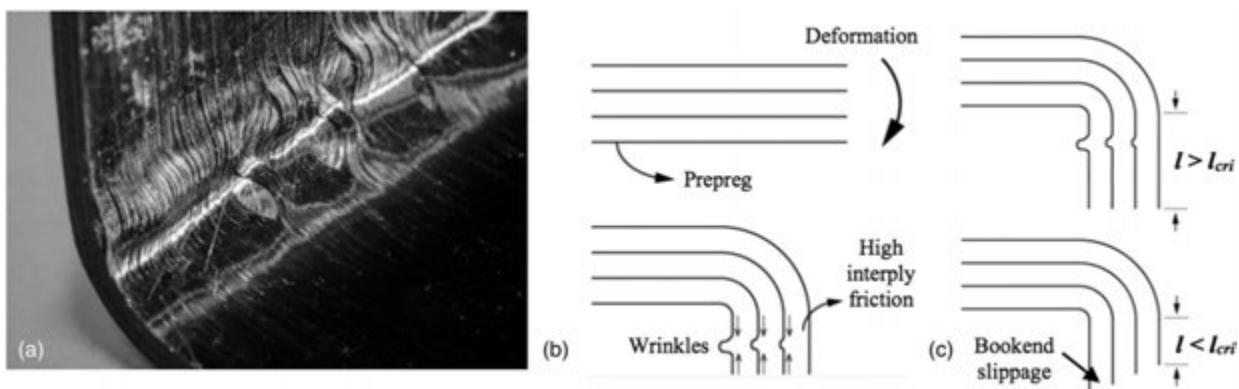


Fig. 8 Defects during HDF: (a) defects at inner radius, schematic diagram of (b) wrinkling mechanism and (c) critical length (l_{cri}). Reproduced from Dodwell, T.J., Butler, R., Hunt, G.W., 2014. Composites Science and Technology 105, 151–159.

process also can be implemented upgrading the existing infrastructure which are used for the automotive industry stamping process offers to meet the composites production for the automobile components specifically, battery packs, cylinders, and other several structural components. Fiber thermoplastic material such as glass fiber (GF), carbon fiber (CF) based polypropylene/polyamide composites can be considered in the stamping process (Zhu *et al.*, 2011).

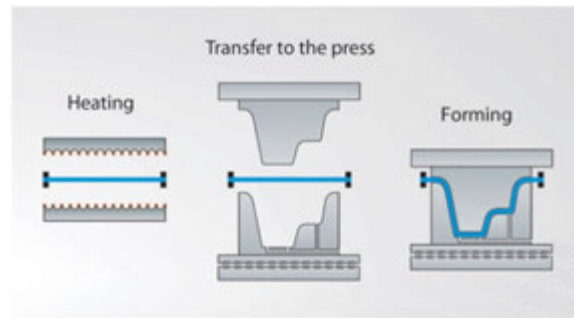


Fig. 9 Composite stamping process.

Initially composites preform sheets are manufactured and laid down to the required stacking sequence. Thus, obtained blanks were cut using a water jet cutting and chemically prepared to stamping operations. Before subjecting to stamping, the blanks were preheated below the melting point of the thermoplastic (matrix) by an external heating source keeping it in infrared (IR) oven. The preheated composite blanks then transformed to preheated molds (50–60°C) and stamped by applying an optimized and controlled pressure as shown in **Fig. 9**. Rapid stamp cooling is applied to the molds to prevent excess deformation and to retain the stamped shapes (Zhu *et al.*, 2011; Peng and Rehman, 2011).

The challenging task of the composite stamping is deformation of fiber laminate which involves interlaminar shear and intralaminar shear. This can be controlled by providing the fiber slipping mechanism at the top and fibers during stamping will move against each other on successive plies. Fiber bridging may occur at the small radius portions of the composites during stamping under high tension forces due to the high stiffness and low elongation properties of the fiber as shown in **Fig. 10** (Trudel-Boucher and Champagne, 2018). The many trial works are requiring to stamp such sharp edge contours and to eliminate defects during mass production.

Resin Transfer Molding (RTM)

Resin Transfer Molding (RTM) method is the one of the most promising and easily adaptable method for the automotive industry. This method has the capability of making the 3D complex parts with close tolerances. The composites manufactured in this technique exhibit high mechanical properties and good surface finish. RTM method also cost effective method and can able to produce miniature components to large components in mass with low tooling cost. **Fig. 11** demonstrates the composites manufacturing using RTM method. The process involves the sequencing the lamination on the one half of the mold and closed with other half. Pressure is applied for the enclosed molds and preform are generated. Suitable resin is injected to preforms with positive gradient pressure through gate points by entrapping the air by vacuum. When the resin is filled completely, the gates are closed and clamped and allowed for the curing. After curing the molds are opened and composites are removed (Gascón *et al.*, 2016; Ashworth *et al.*, 2016).

The process allows to obtain a desired thickness and desired volume fractions of fiber in the composites. During preform stage, microstructure and dimensions of the composites may undergo deformations and induces the residual stresses due to nonlinear viscoelastic effect. These stresses can be relieved during impregnation on the preform and further ensuring of complete impregnation is required to avoid the dry spots areas which makes the poor adhesion of layers and also impart in rough surface and other irregularities consequently poor mechanical properties. The cost of the mold varies and depending on the complexity of the part to be produced and depending process can easily automated depending upon the composite complexity. The viscosity of the injecting resin to the preforms is also important parameter where injection time is directly proportional to viscosity. If the viscosity is higher, then high pumping pressure is required and this may cause the fiber distortion within the preforms (Michaud, 2016; Kang *et al.*, 2000).

The RTM composites ended with some of the defects depending on the resin flow, wettability lead to voids and other dry spots during production which affects the reproducibility and production quality. The failure of the RTM composites mainly depending on the presence of percentage of porosity and these points become the starting points for the initiation and propagations of the cracks. The injected resin experiences the two types of resistances in the preform: One is resistance between the bundles of fiber in macro range and other is within the bundle in micro range (Ferland *et al.*, 1996; Kang *et al.*, 2001). This indicates, preforms are exhibiting two types of permeability's and also because of this there may be potential chances of void formation within the composites. **Fig. 12** clearly demonstrates the mechanism of void formation in a bundle of fiber. During the injection process, the resin usually flows and continue the impregnation around the tows as shown and if air is not trapped or evacuated properly, the formation of voids taken place. This can also be due to the micro pressure drop during the flow. **Fig. 13** shows the relation between phases of manufacturing and its effects on final quality of the product. The relation clearly indicates that resin impregnation and compaction (preform) phases having a greater influence on the formation of dry spots and voids. From this, it can be understood that the manufacturing process is directly influence the final quality of the composites. In addition to this, surface finish of the final composite may also play important role in bringing down or increasing the

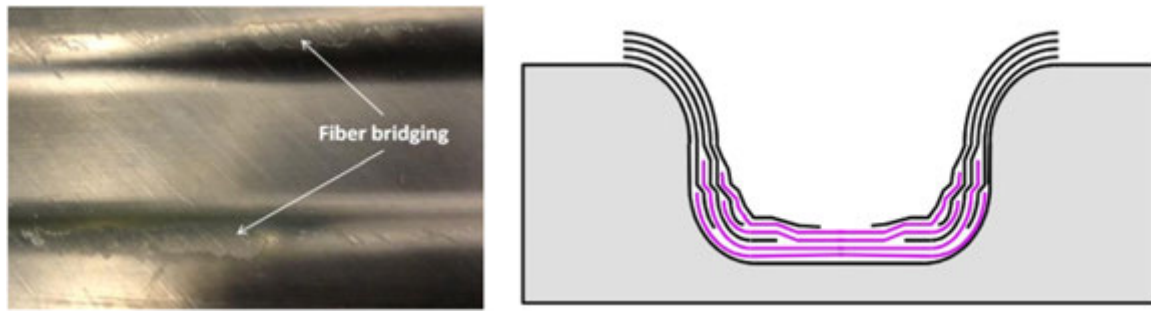


Fig. 10 Fiber bridging on stamped thermo-composite intrusion beam. Reproduced from Trudel-Boucher, D., Champagne, M.F., 2018. Materials Science and Engineering 418, 012127.

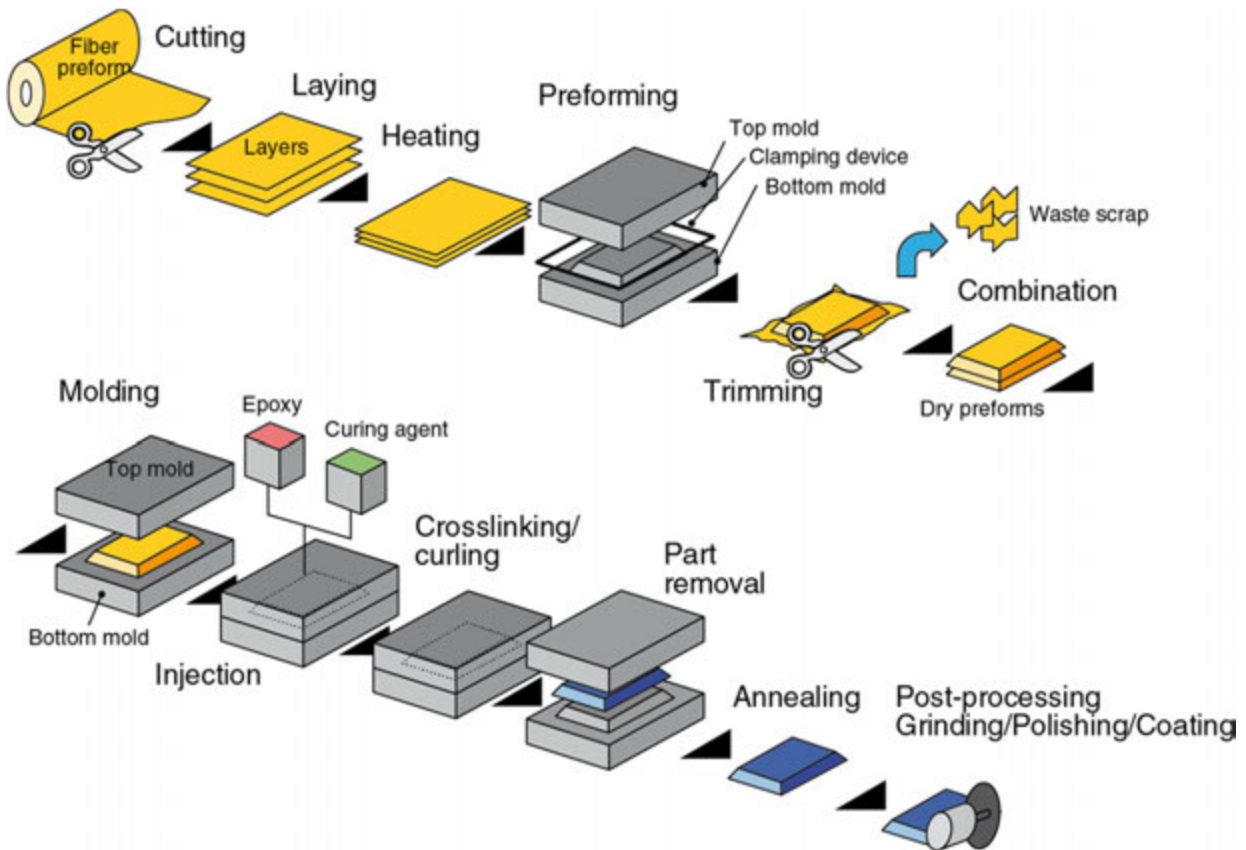


Fig. 11 Sequence of resin transfer molding (RTM) process.

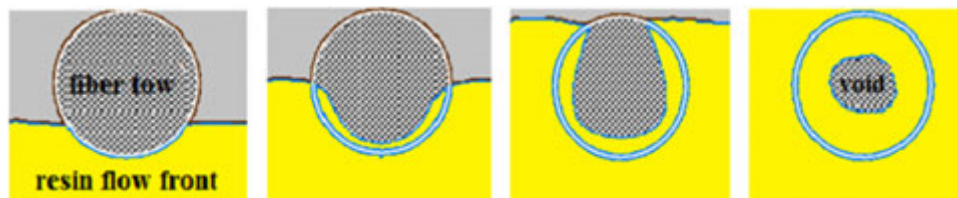


Fig. 12 Demonstration of mechanism of void formation in a fiber bundle. Reproduced from Kang, M.K., Lee, W.I., Hahn, H.T., 2000. Composites Science and Technology 60 (12–13), 2427–2434.

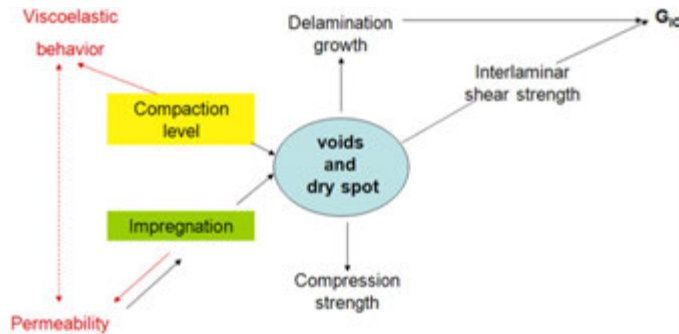


Fig. 13 Effects of manufacturing on RTM final product properties Reproduced from Kang, M.K., Lee, W.I., Hahn, H.T., 2000. Composites Science and Technology 60 (12–13), 2427–2434.

degradation of the composite when expose to air or other environmental conditions. Also, good surface finish of the composite can prevent the penetration of dust or other foreign particle as a consequence, the mechanical properties, and life of the composites can be prevented (Leclerc and Ruiz, 2008; Chen *et al.*, 2001).

Prepeg-Curing Method (PCM)

Prepeg is the composite reinforcement materials that have pre-impregnated with the activated resin including hardener and actuators. The epoxy resin is commonly used to manufacture the prepegs and that are uncured. The prepegs usually cure in oven or ambient cooling depend upon the chemical composition. The time span of the prepeg before its partial curing known as “out life” and the duration in which the prepegs are stored in unusable is called “freezer life” or “shelf-life” (Kumar *et al.*, 2015).

Prepeg manufacturing

Prepegs can be manufacturing in variety methods and the process consist of reinforcing the fiber mechanically with the thermoplastic resin. Some times yarn in unidirectional also used to produce the produce the prepegs (Larco *et al.*, 2017; Fujino *et al.*, 2002). In the manufacturing process, polymer usually dissolved in a solvent to have a lower viscosity and to facilitate fiber to wet and impregnate. In the next stages, impregnated reinforcement is from the solvent made pass through nip rollers which controls the proportion and the aspect ratio. After that impregnated reinforcement pass through over and solvent is dried off. Such obtained prepegs are sandwiched between backing papers, rolled, and stored in freezer to prevent it from the curing.

Prepeg curing

The development of composites structures using Pre-pegs involves several steps. Its requires Mold Preparation, Creation of Templates, Cutting of Prepreg Material, Adding the Backing Ply/Plies, Release of Film and Breather Cloth, Loading the Parts and Positioning the Through- vacuum Bag Connector, Loading into the Oven for Curing and De-molding. Initially mold will be prepared using a suitable material, most of the cases, wax, or chemical release agent are used to as releasing agents. Once after the mold preparation, it's required to prepare the cutting template for the prepeg materials. This process helps in cutting the specific parts accurately from the roll with minimum wastage and these templates can be used repeatedly for succeeding products. Templates can be created using malleable materials or composite products. The next step involves cutting the prepeg materials (Kumar and Mir Safiulla, 2012). This can be done using previously prepared templates called as transfer templates carried out at room temperature. Thus, obtained prepegs are put into the mold by removing the backup films layer and kept inside the breather cloth vacuum bags. Thus, prepared complete set is subjected to curing by keeping it in an oven and before that vacuum leak test is carried out. Once after curing process the composites cooled to room temperature and de-molding is done by removing vacuum bang and breather cloth. The cured parts are trimmed to remove the extra features during fabrication (Vautard *et al.*, 2013). Other procedure like laying the prepegs on to the mold and pressing followed by curing and de-molding is also followed as shown in Fig. 14 to fabricate the composites using prepegs (Fig. 15).

Pre-peg manufacturing is an alternative and effective way to produce a composite compared to autoclave cure technique. This method also provide the economic, technical and environmental benefits compared to conventional production methods. This method also applicable to manufacture of flat laminates in high production rate with defined microstructure and high geometrical efficiency. But only limited compaction pressure to be applied for the prepegs during manufacturing and highly skillset is required to fabricate the complex structures. If the pressure is more, the composite ended with several defects such as corner thickening or corner thinning, voids and delamination's (Fig. 16). This is also required to address with proper curing parameters to avoid the corner geometrical imperfections (Beziers *et al.*, 1996; Grunenfelder *et al.*, 2017).

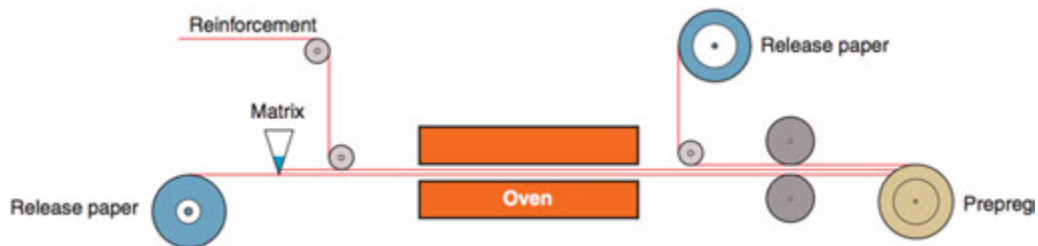


Fig. 14 Schematic of the prepreg manufacturing process. Reproduced from Larco, C., Pahonie, R., Mihaila-Andres, M., 2017. AIP Conference Proceedings. 1836 (1), 020037.

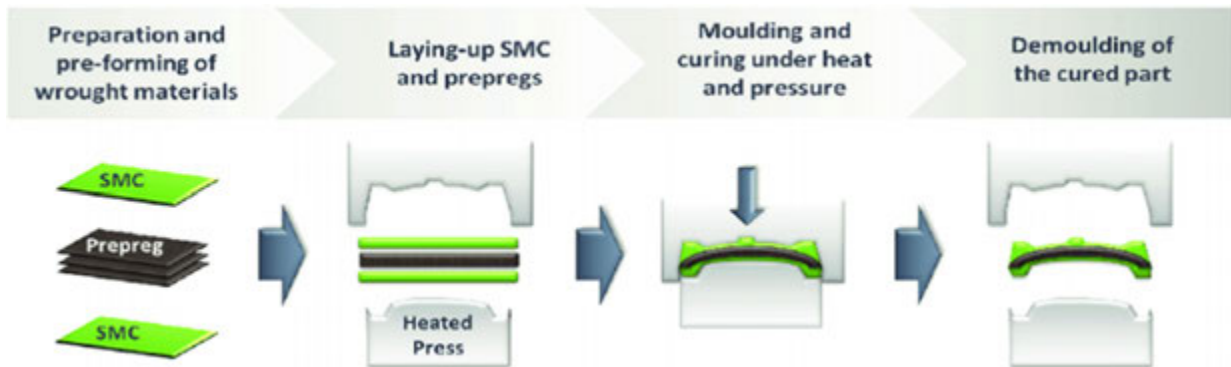


Fig. 15 Prepeg- Curing Method (PCM).

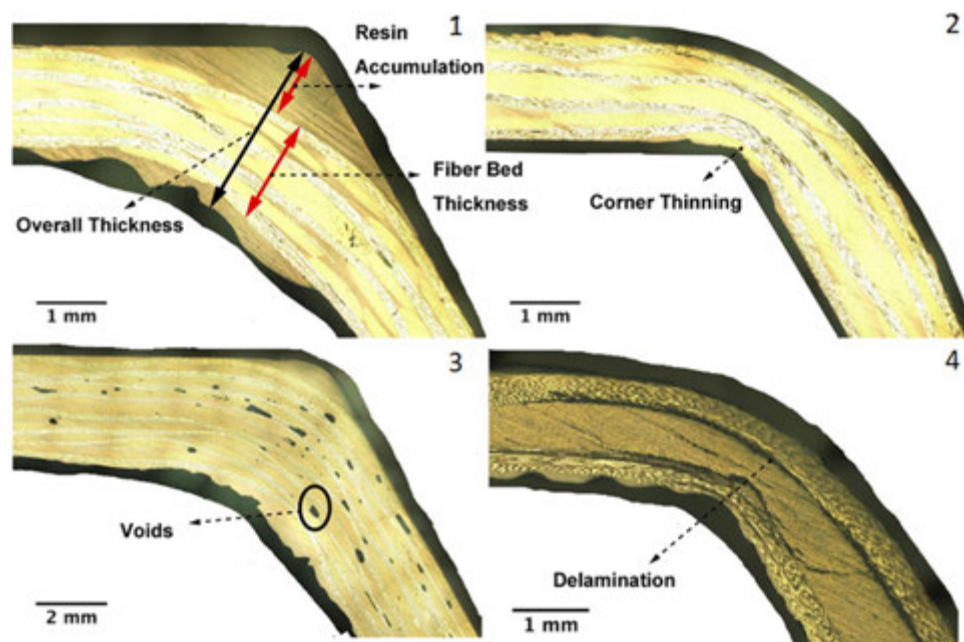


Fig. 16 Defects during prepreg curing: (1) corner thickening, (2) corner thinning, (3) voids, and (4) delamination.

Filament Winding Method (FWM)

Filament winding process is the one of automated method of producing a cylindrical composite structure by winding a filament over the mandrel. The position of the filament will be guided by the machine or robot in two axial or more axes motions as shown in the schematics (Fig. 17). Basically filament winding method is used to manufacture wide range of composites products such as pipes, pipe joints, masts, pressure vessels, storage tanks, etc. The basic filament winding machines consist of mandrel, carriage travel (Hopmann *et al.*, 2019).

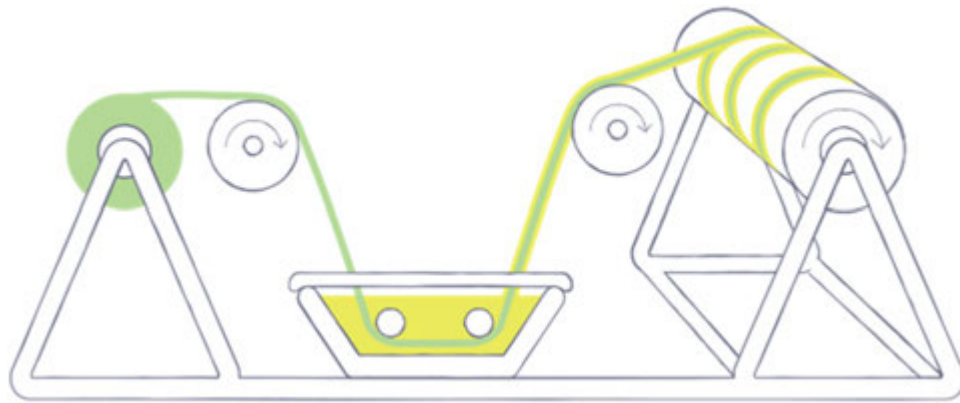


Fig. 17 Schematic of the filament winding process. Reproduced from Akkus, N., Garip, G.E.N.C., 2017. The International Journal of Advanced Manufacturing Technology, 91 (9–12), 3583–3589.

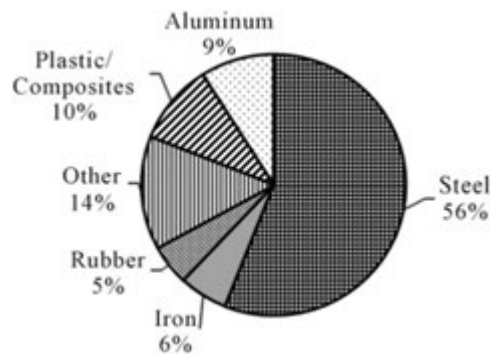


Fig. 18 Various material distribution by weight of standard automotive vehicle. Reproduced from Akkus, N., Garip, G.E.N.C., 2017. The International Journal of Advanced Manufacturing Technology, 91 (9–12), 3583–3589.

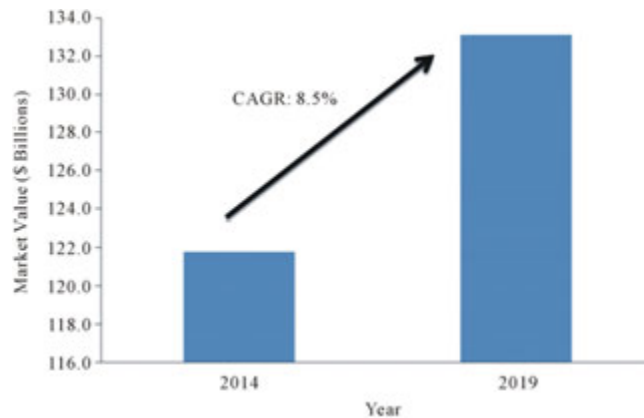


Fig. 19 Increase on compound annual growth rate due to composite market. Reproduced from Pervaiz, M., Panthapulakkal, S., Birat, K.C., Sain, M., Tjong, J., 2016. Materials Sciences and Applications 7 (01), 26.

The machines are available in two axes, four axes and six axes controlling. Two axes controlled machines are limited only to manufacture cylindrical shaped structures, whereas pressure vessel and containers can be produced by using additional radial (cross-feed) axis which is perpendicular to carriage travel in a four axes machines. The machines also available in six axes winding where it is comprised of 3 linear and 3 rotational axes. Usually, machines with more than 2 axes will be having a CNC/computer control and 2 axes will be run usually numeric control. The mandrel with suitable shape and size made up of aluminum or steel with super finish surface (Akkus and Garip, 2017).

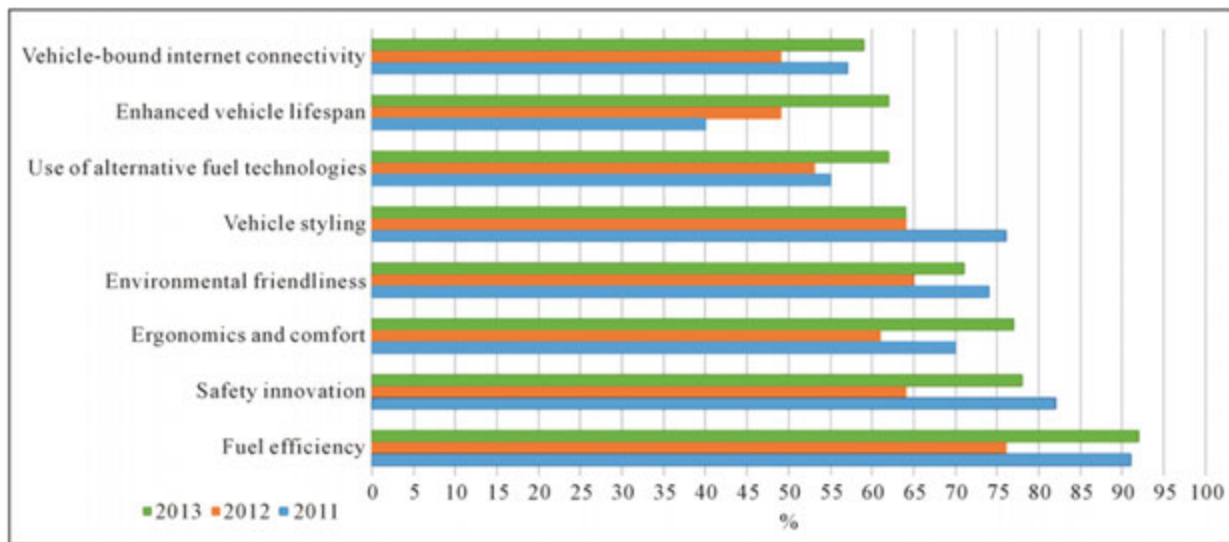


Fig. 20 Priorities areas by the automotive consumers for years 2011–2013. Reproduced from Pervaiz, M., Panthapulakkal, S., Birat, K.C., Sain, M., Tjong, J., 2016. *Materials Sciences and Applications* 7 (01), 26.

Filament winding will be results in high degree fiber loading in various axes which enables the high strengthened hollow cylinders which can also be used in chemical storage, fuel storage, rocket motors cases. The process also makes composites with high strength to weight ratio cylindrical laminates and enables high control of fiber orientations and can be developed close tolerances. Further, the process can be atomized with the less human interruptions.

Composites Automotive Market Trends and Priorities

The car is made-up of various material ranging from metal, glass and other plastic components. The data shown in Fig. 18 is the evident that metal exhibiting an important role compare all other materials and still research is underway to finding new class or alternate materials to reduce the overall weight for the automotive vehicles. The scope for alternate and high strengthen with low density and cost effective materials is the one of thrust area in materials research specifically substitution for the steel and chassis materials (Akkus and Garip, 2017; Pervaiz *et al.*, 2016). All over the globe, many industries involved to produce high scale commercial products in this area. Other side, aluminum, magnesium, and manganese also trending materials for lightweight applications but when it comes to density, cost, and environmental aspects, becoming a challenge to compete.

In recent decades, advanced polymer based composites have taken a front role as alternative and light weight materials application for the automotive parts. The trend of increase in composites attention due to the high strength and rigidity and enabling to manufacture conventionally. The main advantage of consideration of these materials is in reduction of weight, about 30%–40% compare to conventional metals and implementation of these as alternate can reduce the overall vehicle weight up to 10%–12% (Das, 2011). Further, investment for these materials fabrication will be reduced to 50%–55% compare to current manufacturing technology. Further most of the assembly process can replace with single component with increased efficiency (Jacob, 2004; Pervaiz *et al.*, 2016) and important motivation is using of naturally available materials as semi finished products in vehicles will attract much more in the globe in terms of green go. With this advantages and other benefits, the composite adoption become increased and there by proportionally increase in Compound annual growth rate (CAGR) by 8.5% till 2019 (Fig. 19). This trend also represents the demand for light weight materials, specifically composite materials in various sector applications.

Global warming issues is another factor which is affecting the natural disaster drastically. In order to prevent these catastrophic disaster, these days' consumers also changed the preferences and priorities. This awareness makes car manufactures to deliver high efficiency and eco-friendly vehicles to satisfy the consumers. Fig. 20 shows the top priorities of consumers assessed by top automotive industry globally (Pervaiz *et al.*, 2016). In order to satisfy the customer needs, transport industry now leading the major research in light weight vehicles and meeting the strict environmental legislations.

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Further Reading

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Routes for the Joining of Metal Matrix Composite Materials

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Introduction

Metal matrix composites (MMCs) are preferred in many applications in aerospace, automotive, and marine industries due to its better specific characteristic than conventional alloys. Al, Mg, Cu, and Ti are mostly preferred as matrix material. Various ceramic particles such as oxides, carbides, nitrides, borides, and intermetallics are used as reinforcements for MMCs. The successful incorporation of ceramic particles both in-situ or ex situ process into the matrix alloy and achieving good bonding between them will help to enhance the properties. In view of effective utilization of these composites, they are in need to join with similar or dissimilar components. The components made of MMCs used in spacecraft, electronic instrument racks, turbocharger, and automotive drive shafts are to be fitted ([Matthews et al., 2016](#); [Jahangiri et al., 2012](#)). The mechanical fasteners are normally not feasible, due to stress concentrations. Welded components and structures are widely used in almost all industries, and as such, weld integrity is highly necessary for the adequate and reliable performance of components.

The challenges depend on the kind of matrix materials used, type of reinforcements, complexity of geometry and similar and dissimilar joints. The difficulties associated with conventional welding are higher viscosity of MMC melts, segregation during solidification, reinforcement/matrix interactions, and evolution of occluded gases ([Ellis, 1996](#)). It is important to ensure that the joining process does not react adversely with the MMC so that properties are reduced in the joint region. MMCs can be joined by a variety of methods, but care is needed to avoid unwanted reactions, particularly with fusion processes, and destruction of the reinforcement in the joint region. The joining technology of MMCs is a greater challenge to the potential industrial applications.

The different properties of components in composite materials, the joining of MMCs does indeed present a challenge, especially in terms of their poor weldability with conventional fusion welding processes ([Chen et al., 2009](#)). In addition, other joining methods, such as the mechanical bonding of Al-Mg₂Si materials, usually result in excessive tool wear and are relatively expensive. Non-traditional welding processes like laser beam and friction stir welding are more effective and expensive techniques.

Generally, the welding of composites is classified into two groups: fusion welding methods and solid-state welding methods. The fusion welding problems such as high viscosity, uncontrolled solidification, the presence of porosity, the formation of excess eutectic, and deleterious phases and adverse reactions cause micro- and macro defects in the welding and reduce the welding capability. Also, the properties of the parent material will change owing to the high temperature at the fusion welds ([Orhan, 2015](#)). [Chen et al. \(2009\)](#) reported that in the fusion zone of conventional welding, the deleterious reactions between the reinforcement particles and the liquid metal, and an irregular redistribution of reinforcement particles frequently occurred, which greatly limits the weldability of aluminum-based MMCs. Recent studies have revealed that, because of possible joining problems in fusion welding methods, it is more advantageous to weld MMCs by using solid-state welding methods. In order to enable the wide utilization of MMCs, effective joining methods such as solid state and fusion processes become of practical importance ([Ni et al., 2013](#)). In this article, particular attention is paid to surveys on the weldability of MMCs using fusion welding processes such as gas tungsten arc welding, laser beam welding, electron beam welding, and solid-state welding processes like friction welding and friction stir welding.

Gas Tungsten Arc Welding

Gas tungsten arc welding (GTAW), also known as tungsten inert gas (TIG) welding, is an arc welding process which fuses metals by heating them between a non-consumable tungsten electrode and the base metal, while a continuous envelope of inert gas flows out around the tungsten electrode. With the technological developments made in TIG equipment, it is now the most versatile of all the fusion welding processes. It can be used to join most metals like aluminum and magnesium and their alloys, alloyed steels, carbon steels, stainless steels, copper, nickel and nickel alloys, titanium, tin, silicon, aluminum bronzes, and cast iron. Joining of aluminum and its alloys by GTAW welding is well known, but the presence of ceramic particles in the composite can present problems caused by: difference in thermal expansion between ceramic particles and the aluminum-alloy matrix, higher melting points of ceramics than of matrix, high arc energy that leads to the degradation of ceramic particles and consequent lowering of the mechanical properties of the joint, generation of surface reaction between the reinforcement and liquid matrix material. It is therefore necessary to introduce into the weld a filler material of good flowing power, which is also compatible with the parent metal and possesses good wettability of the reinforcing phase.

Normal practice with aluminum alloys is to use alternating current to break up the surface oxide film and obtain satisfactory fusion, and this is the case also with Al-based MMCs. [Ellis \(1996\)](#) indicated that both matrix-particle reactions and particle segregation can be reduced with careful choice of consumable. The use of Si-rich Al fillers increases the wettability of the SiC in an Al matrix, enhancing mixing of the plate and filler materials. Mg containing wires (ER5356) is preferred for Al₂O₃ reinforced Al MMCs, which prevents the Al₂O₃ from poor wetting and clumping. Typical welding parameters and mechanical properties of TIG welded 2080/20SiCp and 7475/20SiCp MMC are given in [Table 1](#).

Table 1 Mechanical properties of parent and welded composites

Material	Condition	Yield strength (0.2 MPa)	Tensile strength (MPa)	Elongation (%)
6% SiC _p	As received	123	211	4
	Weld – 1	74	100.7	–
	Weld – 2	67	75.7	–
13% SiC _p	As received	151	251	3
	Weld – 3	104	152	–
	Weld – 4	92	132	–
20% SiC _p	As received	183	305	2.3
	Weld – 5	107	137	–
	Weld – 6	67	67.5	–

Note: Urena, M.D., Escalera, L.G., 2000. Influence of interface reactions on fracture mechanisms in TIG arc-welded aluminium matrix composites. *Composites Science and Technology* 60, 613–622.

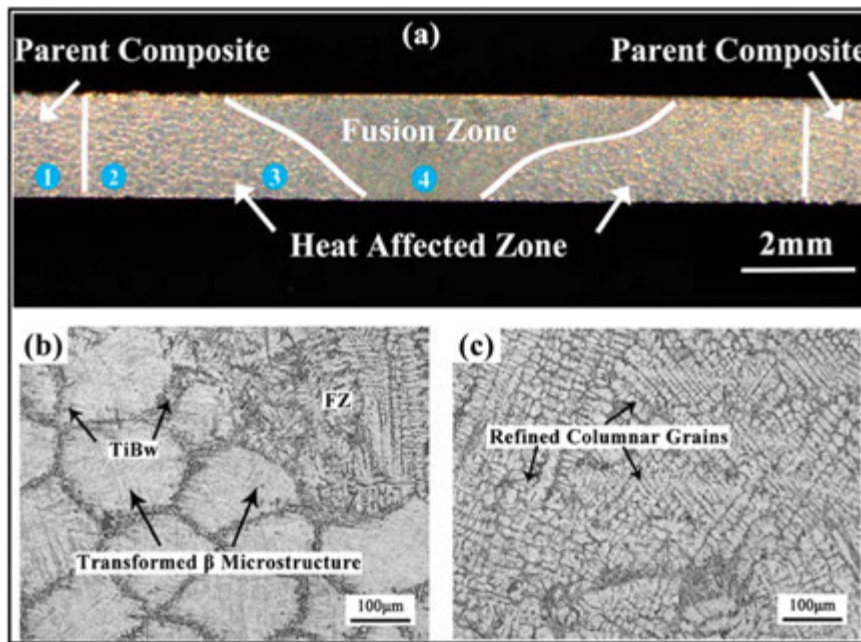


Fig. 1 Microstructures of gas tungsten arc welded TiBw/Ti6Al4V composites: (a) macrograph of the cross-section, (b) HAZ OM micrograph and (c) FZ OM micrograph. Reproduced from Huang, L., Duan, T., An, Q., *et al.*, 2018. Gas tungsten arc welding of network structured titanium matrix composite. *Science and Technology of Welding and Joining* 23 (5), 357–364.

Jahangiri *et al.* (2012) studied the welding feasibility of an Al-(15 wt% and 20 wt%) Mg₂Si in-situ composites using TIG by Al-Si filler metal. The increased welding current from 80 to 100 amp, decreased the formed Mg₂Si reinforcement and caused to dilute the parent composites. The finer pseudo-eutectic phase was observed with fast cooling rate during the joint solidification. Four different regions of microstructure such as the fusion zone, the interface region, HAZ and unaffected areas were observed. The HAZ will increase with an increase in the welding current. The Mg₂Si particles are distributed at the top and the root of the weld. Huang *et al.* (2018) studied the TIG welding of insitu 5 vol% TiBw/Ti6Al4V composite using 300A AC-TIG welding source. The novel network microstructure and the morphology of the TiBw were maintained in the HAZ and the interface between the HAZ and FZ is clear without visible welding defects as shown in Fig. 1. The HAZ consists of transformed β microstructure and little primary α phase, while the FZ is composed of refined columnar Ti6Al4V grains and minimized TiB_w reinforcement with a refined network microstructure. The average hardness value of 630 HV in FZ and 580 HV at HAZ is observed than that of the parent composites (430 HV). The hardness and the tensile strength of the welded composite rise with the increased heat input, which can be attributed to the smaller micro networks, refined and more homogeneous distribution of the TiBw in the FZ, and the enlarged fraction of the transformed β phase. The hardness value of MMCs decreased by increasing the current from 80 to 100 amp. Low heat inputs provided higher weld strengths and better weld integrity.

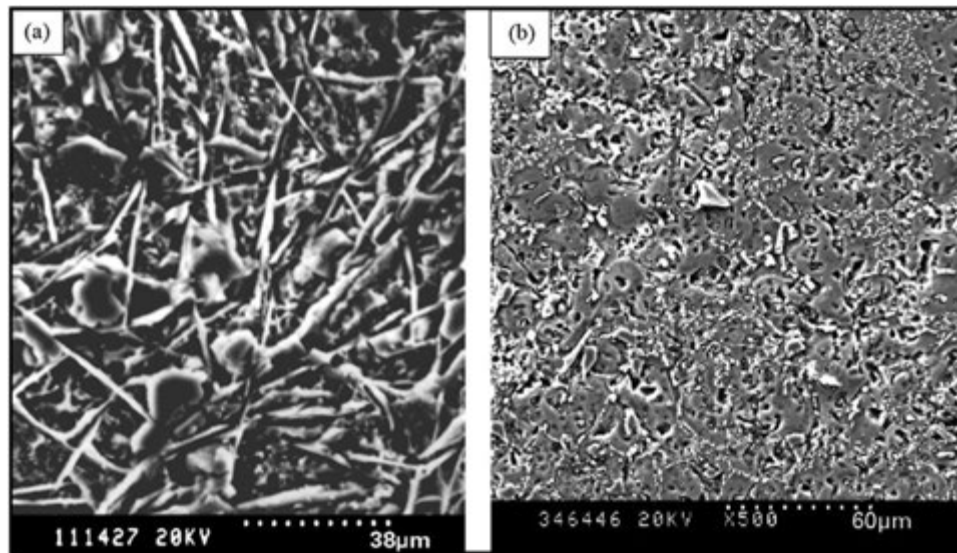


Fig. 2 Microstructure of TIG welded AA6061/SiC composite joint: (a) with and (b) without Al-Si filler. Reproduced from Xi-he, W., Ji-tai, N., Shao-kang, G., Le-jun, W., Dong-feng, C., 2009. Investigation on TIG welding of SiCp-reinforced aluminum-matrix composite using mixed shielding gas and Al-Si filler. *Materials Science and Engineering A* 499, 106–110.

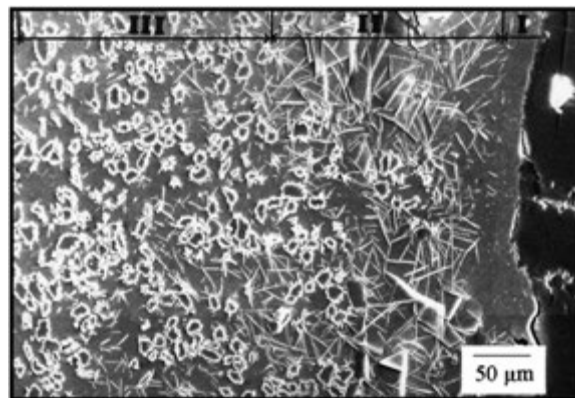


Fig. 3 TIG welded AA2014/SiC13_p composite showing different zones of Al-SiC reaction. Reproduced from Urena, M.D., Escalera, L.G., 2000. Influence of interface reactions on fracture mechanisms in TIG arc-welded aluminium matrix composites. *Composites Science and Technology* 60, 613–622.

Xi-he *et al.* (2009) welded 6061/15 vol% SiC_p composites plate of 60 mm × 30 mm × 3 mm using single electric arc discharge TIG WSE-315 machine on one face with filler of Al-Si alloy. Optical micrograph shown in Fig. 2 revealed the presence of more non-uniform distribution of SiC particles in the weld center. Addition of Al-Si filler greatly suppressed the interface reaction between SiC and matrix. The average welded joint strength of 70% (240 MPa) is achieved than parent composites (271 MPa).

Pichumani *et al.* (2018) observed fine grain weld microstructure with higher micro hardness at weld center while using activated TIG welding on Al – 8% SiC composite 5 mm plate with SiO₂ and ATIG – TiO₂ fluxes. Jayashree *et al.* (2018) used single pass TIG welding current of 220 A, a speed of 140 mm/min, and a gas flow rate of 14 L/min on AA6061–0, 8, and 10 wt% SiC composites using an ER5356-grade filler material and resulted the increase of 25%–28% tensile strength for peak-age-hardened specimens at 100°C. Urena and Escalera (2000) reported the TIG arc-welding of 4-mm thick sheets of AA2014/SiC/X (where X is 6, 13 and 20 vol%) MMCs. The three different zones of weld formation (Fig. 3) such as: (1) top zone with complete dissolution of the SiC reinforcement and precipitation of Al₄C₃ flakes into the molten aluminum; (2) intermediate zone of partial dissolution of the particles and formation of shorter Al₄C₃ flakes; (3) bottom zone with formation of Al₄C₃ platelet crystal which nucleated and grew on preferential planes of the SiC particles. The formation of interfacial Al₄C₃, reduced the strength of the composites.

Generally pulsed current gas tungsten arc welding are obtaining grain refinement in weld fusion zones and improvement in weld mechanical properties of Ti alloys (Mao *et al.*, 2014). It produces reduced width of heat affected zone, refinement of fusion zone grain size and substructure, control of segregation, etc., as shown in Fig. 4. Titanium matrix with TiBw and La₂O₃ particle

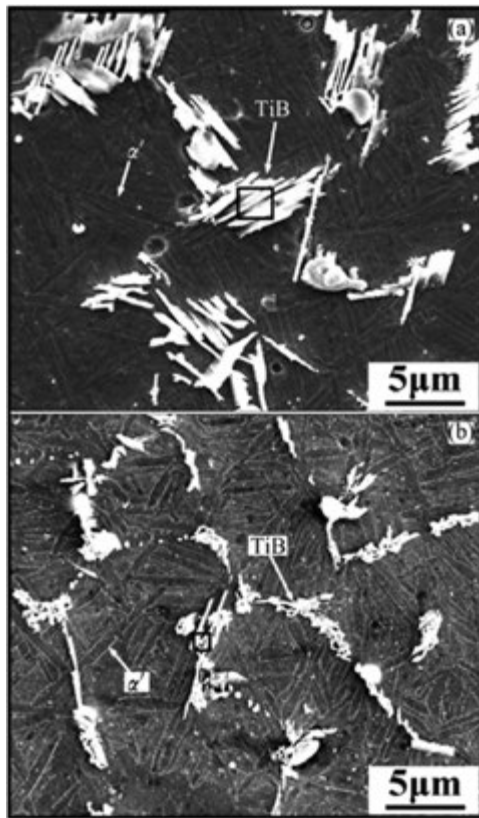


Fig. 4 Enlarged SEM images of FZ of Ti/TiB_w composite in unpulsed (a) and pulsed (b) conditions. Reproduced from Mao, J.-W., Lü, W.-J., Wang, L.-Q., Zhang, D., Qin, J.-N., 2014. Microstructure and mechanical properties of GTA weldments of titanium matrix composites prepared with or without current pulsing. Transactions of Nonferrous Metals Society of China 24, 1393–1399

Table 2 Mechanical Properties of WM, WJ, and BM

<i>Tensile specimens</i>	<i>Tensile strength, MPa</i>	<i>Elongation, %</i>
Weld metal	140–190	1–3
Welded joint	130–160	0–1
Base metal	150–180	1–2

Note: Xuan, Z.Z., Gu, X.Y., Zhong, R., Sun, D.Q., 2010. Microstructures and mechanical properties of tungsten inert gas arc welded magnesium metal matrix composite (TiCp/AZ91D). Materials Science and Technology 26 (12), 1513–1517.

reinforced MMCs enhanced the welded strength of pulsed joint is approximately by 3% and 8% at room and elevated temperature respectively compared with the unpulsed joints.

TiC_p/AZ91D composites was joined by TIG welding with filler metal by Xuan *et al.* (2010). TiC particulates are clearly visible in the weld metal (WM), and were not melted during welding due to high melting temperature of TiC. TiC particulates were distributed at primary α -Mg grain boundaries and some agglomerates of TiC particulates are entrapped inside α -Mg grains, which could be rationalized in terms of pushing and engulfment of the particulates at the solidification interface. Compared with the BM, the WM has finer grain size due to rapid cooling rates of WM. WM has higher hardness compared with the BM due to grain refining of WM. In the joint, the lowest hardness appears in HAZ. It is mainly associated with grain coarsening of HAZ. The mechanical properties of WM, WJ, and BM are listed in Table 2 (Xuan *et al.*, 2010).

Mao *et al.* (2013) reported the gas tungsten arc welding of in-situ reinforced TiB_w-titanium matrix composites. The weld zone had a refinement in microstructure and TiB_w exhibited smaller size and dispersed distribution, forming a novel network structure in the weld. The welded strengths of TMCs joint are more than 85% of the base metal strength. Grabian and Wysocki (2007) reported the manual TIG-welding of metallic composites of AlSi/SiC using fillers containing zirconium oxide which influences the size reduction of grains in the weld. No products of surface reactions between the matrix and Al₃C₄ reinforcement were detected.

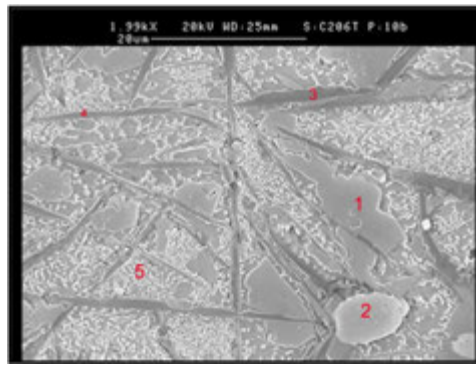


Fig. 5 SEM micrograph of region 1: in the Si enriched matrix (5), with an eutectic structure, occasional SiC (2) is visible, as well as Al_4C_3 needles (3) and (4), and crystals of primary Si (1). Reproduced from Bassani, P., Capello, E., Colombo, D., Previtali, B., Vedani, M., 2007. Effect of process parameters on bead properties of A359/SiC MMCs welded by laser. Composites: Part A 38, 1089–1098

Laser Beam Welding

Laser beam welding is a fusion welding process in which two metal pieces are joined together by the use of laser. The laser beam provides a concentrated heat source, focused to the cavity between the two metal pieces to be joined. The process is frequently used in high volume applications using automation, as in the automotive industry. It is based on keyhole or penetration mode welding. The main advantage of laser welding, due to its high energy density, is its ability to melt the area located at the edges of the joint, without affecting a large area of the part. Laser welding is a high-power-density fusion-welding process that produces high aspect ratio welds with a relatively low heat input compared with arc-welding processes. Furthermore, laser welding can be performed “out of vacuum” and the fiber-optic delivery of near-infrared solid-state laser beams provides increased flexibility compared with other joining technologies. Consequently, laser welding may be considered as a principal candidate for the production of metallic aerospace components for high-performance environments. Laser beam is one of the most potential heat sources for joining metal matrix composites. Due to the focusable high intensity heat source, it is increasingly used in many industries. In comparison with conventional arc welding techniques, the deep and narrow fusion zone in laser welding produces a much smaller heat affected zone and results in less thermal distortions and mechanical property reductions (Guo *et al.*, 2012b). The application of laser welding for joining MMCs reinforced with ceramic particles has been reported (Meng *et al.*, 2013).

Bassani *et al.* (2007) used two different laser sources for key-hole and conduction laser welding of A356–20% SiC composite. In keyhole laser welding (CO_2 laser welding) microstructural investigations confirmed the formation of Al_4C_3 by SiC dissolution in Fig. 5. Al_4C_3 formation results in a strong increase of hardness that dramatically reduces the toughness of the bead. In conduction laser welding (diode laser), the Al_4C_3 formation seems to be negligible.

Guo *et al.* (2012a) used a robotized Nd: YAG laser welding equipment for joining 4.3 mm thick plates of AA1100–16 vol% B_4C MMCs without any filler, with Ti foil and with Ti filler wire. Joint efficiency of 63% is obtained for the laser welding of MMCs without filler material. In the weld zone, most B_4C particles are decomposed into needle-like AlB_2 and Al_3BC phases. The joint efficiency has increased to 75% with the addition of 150 μm Ti foil. An appropriate addition of Ti concentration may further improve the mechanical properties of the joints. With Ti addition, TiB_2 , TiC , and Al_3Ti phases are formed in the laser weld zone instead of needle-like AlB_2 and Al_3BC phases. Fig. 6(a) shows a typical macro-view of joints without filler indicating that a sound joint can be obtained. The base material consists of aluminum matrix and B_4C particles which are uniformly distributed in the matrix (Fig. 6(b)), while the laser weld zone consists of a large number of needle-like phases and some B_4C residues (Fig. 6(c) and (d)).

Guo (2010) studied the effect of in-situ reaction on the microstructure of Nd: YAG laser welded joints of aluminum matrix composite SiCp/AlSi7Mg. The microstructure (Fig. 7) of the traditional Nd: YAG laser weld without filler shows that there were lots of acicular Al_4C_3 particles in the weld, which led to a low joint tensile strength of 91 MPa (about 37.9% of parent AMC).

Meng *et al.* (2013) used 15 kW CO_2 laser welding system with a spot diameter of 0.8 mm to weld the TiB_2 –ZL101 composite. The XRD pattern (Fig. 8) shows the possibility of the presence of Al_3Ti , B_2O_3 , AlB_{12} , and TiO_2 in the weld seam. It illustrates that TiB_2 particles are evolved into TiO_2 and B_2O_3 through the reaction with oxygen molecules in the laser welding process. With increasing the temperature, Ti and B ions are released from the broken Ti–B covalent bonds and diffuses into liquid Al, which causes the formation of AlB_{12} and Al_3Ti in the reaction with Al matrix.

Guo *et al.* (2012b) reported that the comparison with arc welding techniques, the deep and narrow fusion zones associated with laser welding can result in smaller heat affected zones, and therefore fewer thermal distortions and mechanical property changes. Wang *et al.* (2007) used pulsed Nd: YAG laser for welding of 12 vol% SiC particulate-reinforced magnesium composite. The increase in laser beam diameter from 1.0 mm to 1.5 mm effectively avoided severe burning and evaporation. Sound laser-welded seam was produced by suitably choosing a laser scanning velocity of 150 mm min^{-1} and the tensile strength of the seams reached about 88 MPa.

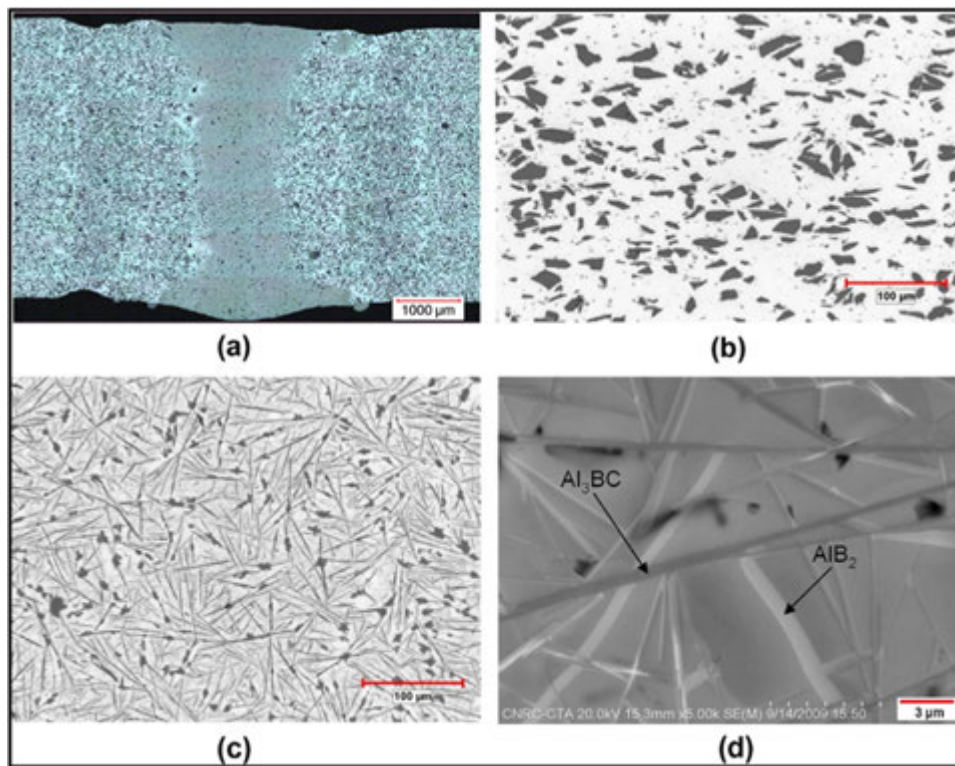


Fig. 6 Images showing typical microstructures of laser welded AA1100/B₄C MMCs: (a) macro-view of the laser joint, (b) base material, (c) weld zone under OM, and (d) weld zone under SEM. Reproduced from Guo, J., Gougeon, P., Chen, X.-G., 2012a. Study on laser welding of AA1100-16 vol% B₄C metal–matrix composites. Composites: Part B 43, 2400–2408.

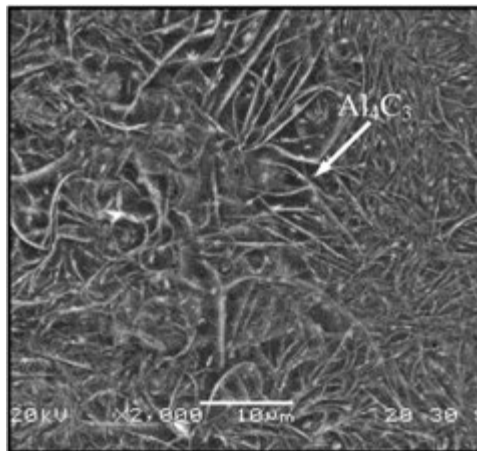


Fig. 7 Microstructure of Nd:YAG Laser welded SiC_p/AlSi7Mg MMC. Reproduced from Guo, K.W., 2010. Influence of in situ reaction on the microstructure of SiC_p/AlSi7Mg welded by Nd: Yag laser with Ti filler. Journal of Materials Engineering and Performance 19, 52–58.

Electron Beam Welding

Electron beam welding (EBW) is a fusion welding process utilizing a heat generated by a beam of high energy electrons. The electrons strike the work piece and their kinetic energy converts into thermal energy heating the metal so that the edges of work piece are fused and joined together forming a weld after solidification. EBW is often performed under vacuum conditions to prevent dissipation of the electron beam. High power electron beam systems for welding are used in the aerospace, automotive, defense, semiconductor, medical, nuclear, oil and gas, power generation, and a variety of other industries. Today's aircraft have

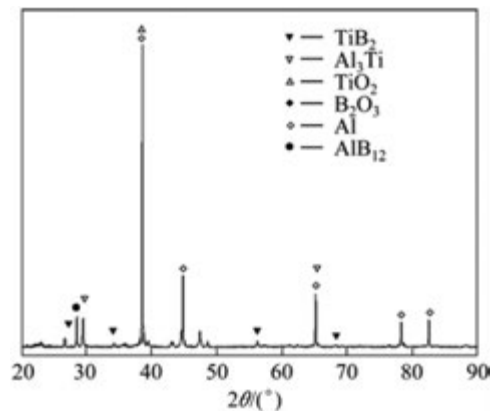


Fig. 8 XRD pattern of weld seam of CO₂ laser welded TiB₂ – ZL101 composites. Reproduced from Meng, C., Cui, H.-C., Lu, F.-G., Tang, X.-H., 2013. Evolution behavior of TiB₂ particles during laser welding on aluminum metal matrix composites reinforced with particles. Transactions of Nonferrous Metals Society of China 23, 1543–1548.

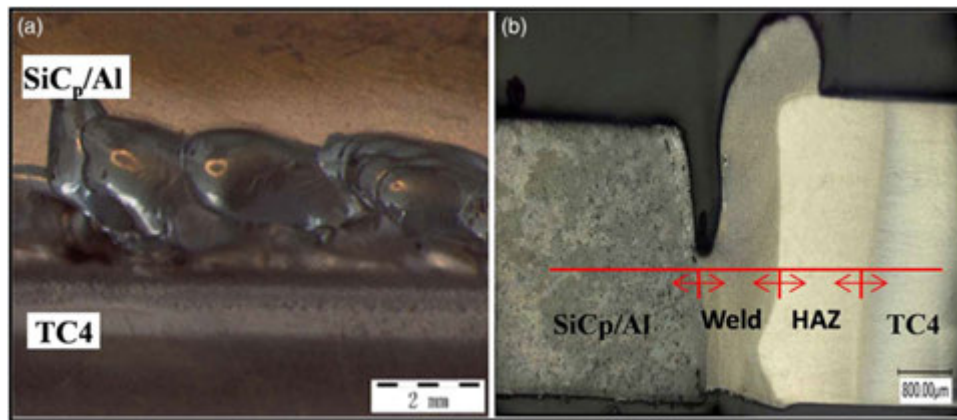


Fig. 9 Weld appearance after non-deviated welding (optical images) (a) façade side of the weld; (b) cross section of the weld. Reproduced from Chen, G.Q., Zhang, B.G., Liu, L.Y., Feng, J.C., 2015. Electron beam welding of SiCp/Al composite to Ti-6Al-4V. Materials Research Innovations 19 (Suppl 5), S5-1309.

components that were manufactured using EBW. The welding of composites has become a hot topic, involving most welding methods. In EBW, one of the key factors of successfully welding SiCp/Al composites is to avoid the decomposition of SiC during the welding process. Hai-chao *et al.* (2010) reported that if electron beam is controlled to move in a circular mode during the welding process, it will induce the stirring effect on the molten pool as it is beneficial to decrease the pores and promote the homogeneous distribution of particles. Moreover, pulsed electron, avoiding the continuous movement of keyhole, is also beneficial to the stability of keyhole. Huang *et al.* (2001) reported that the energy absorption for the electron beam under vacuum did not show apparent differences in the 6061 Al or composites. Only the melting efficiency increased with increasing SiC content.

Chen *et al.* (2015) studied the electron beam welding of SiCp/Al composite and Ti-6Al-4V with a welding speed of 300 mm/min. The results showed that the weld appearance and mechanical properties were poor when the heat source was located at the middle of the butt joint. It is presented in Fig. 9. A well-formed joint with a tensile strength of 108.9 MPa, was obtained when the heat source was deviated by 0.3 mm toward the Ti-6Al-4V side.

Storjohann *et al.* (2005) presented the optical microstructures of the fusion-welded Al-Al₂O₃ and SiC composites at different magnifications as shown in Figs. 10 and 11. The hardness of the Al-Al₂O₃ composite BM is slightly softer (100–140 HV) than that of the Al-SiC composite (180–190 HV) BM. The BM and HAZ regions occasionally exhibit large hardness, due to the preferential sampling of a large volume fraction of reinforcements.

Kun *et al.* (2011) investigated the welding property of TiB₂/ZL101 composite using electron beam (EB) welding experimental system with a function generator. Table 3 shows some welding parameters used in this experiment. Cross-section and surface appearance of EB welds made at different heat inputs is shown in Fig. 12. The full penetration of the plate just occurs under EB power of 2340 W (sample 3), as shown in Fig. 12(c) and (d). In the tests, all the depth-to-width ratios were above 2.5, and HAZ was very narrow because beam diameter of the EB was only 0.1 mm. When the power was increased to 2.8 kW, the excessive penetration occurs, as shown in Fig. 12(e) and (f).

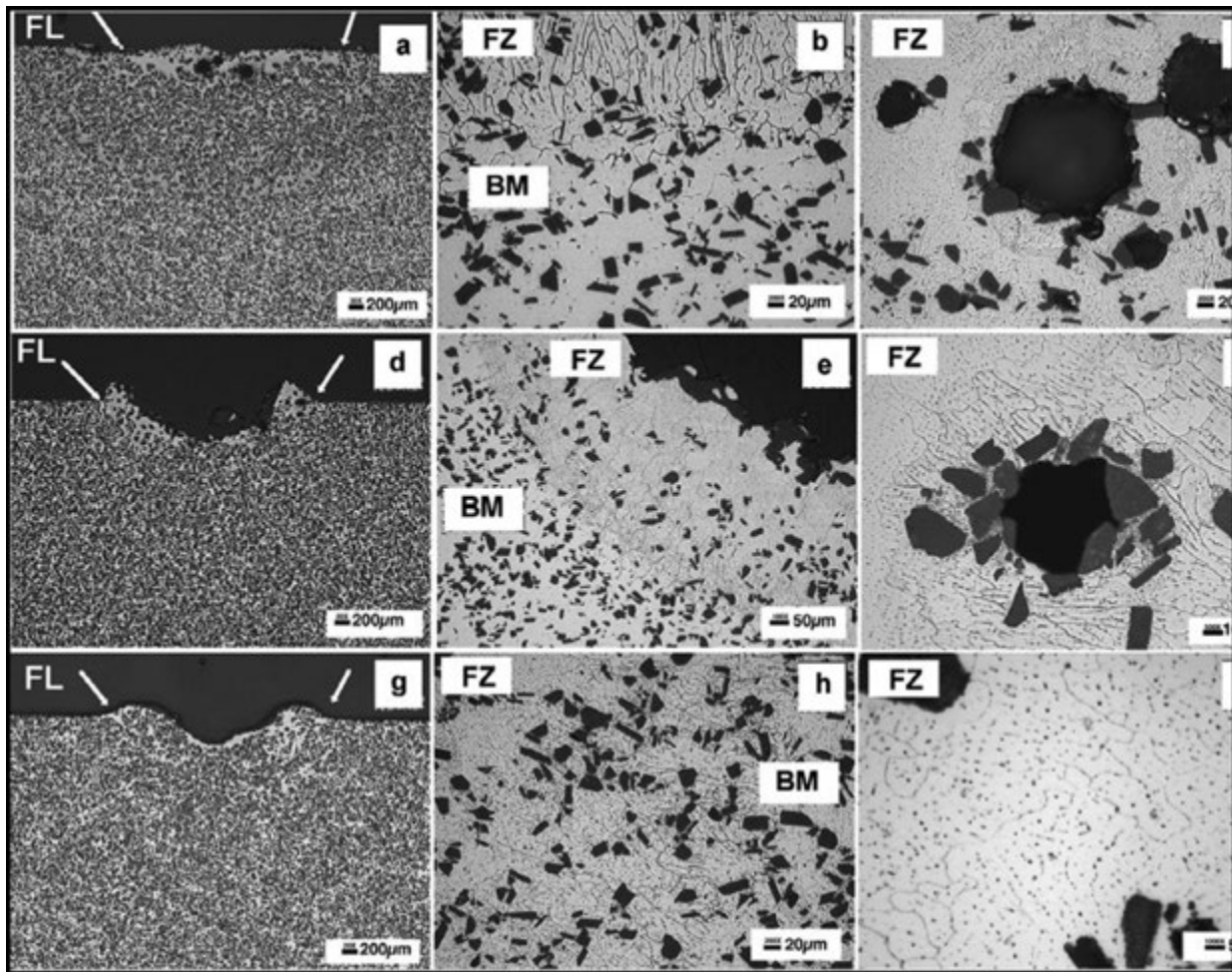


Fig. 10 Optical micrographs of fusion welds made with different welding processes on Al-Al₂O₃ composites are compared: (a) through (c) the GTA welds, (d) through (f) the EB welds, and (g) through (i) the LB welds. Reproduced from Storjohann, D., Barabash, O.M., Babu, S.S., David, S.A., Sklad, P.S., Bloom, E.E., 2005. Fusion and friction stir welding of aluminum-metal-matrix composites. *Metallurgical and Materials Transactions A* 36, 3237.

Huang *et al.* (2001) studied the welding characteristics of a fine-grained 6061 Al and three 6061/1%, 5%, and 20% SiC composites under high energy electron beam welding (EBW) and laser beam welding. In the reinforced composites, the fusion zone contained the once fully melted matrix and fully reacted SiC, and the heat affected zone (HAZ) contained the partially melted matrix and nearly unreacted SiC. This effect was particularly apparent in the 20% SiC composite. With increasing SiC content from 0 to 20 pct, the reflection of the laser beam decreased, and the melt viscosity increased due to the increasing amount of Al₄C₃ compounds. For the HRSR fine-grained 6061/20 pct SiC composite, there formed a sharp V-notch under EBW. The high viscosity or low fluidity of the melt inside the fusion zone of 6061/20 pct SiC resulted in incomplete backfill and notch formation. The size of the Al₄C₃ plates ranged within 15–50 µm, and the thickness was typically less than 1 µm, as shown in the enlarged OM micrograph of Fig. 13.

The microstructure of the EB welds in SiC/LD2 made at different heat inputs is shown in Fig. 14 (Chen *et al.*, 2006). The weld microstructure made at a heat input of 30 J/mm mainly consists of SiC and Al matrix. The Al matrix possesses a very fine cellular solidification structure because of high cooling rate. Compared with the particles in the as received composite, the surface of survived SiC particle in the fusion zone is much coarser. The weld made at a heat input of 36 J/mm showed small sized needle precipitates only at top center in Fig. 14(b).

Friction Welding

Friction welding is a solid-state welding process. The coalescence is caused by the heat generated through friction at the rubbing surfaces, which raises the temperature at the interface high enough to cause the two surfaces to be forged together under high pressure. Friction welding is preferred during the fabrication process, since joints are created rapidly and have consistent

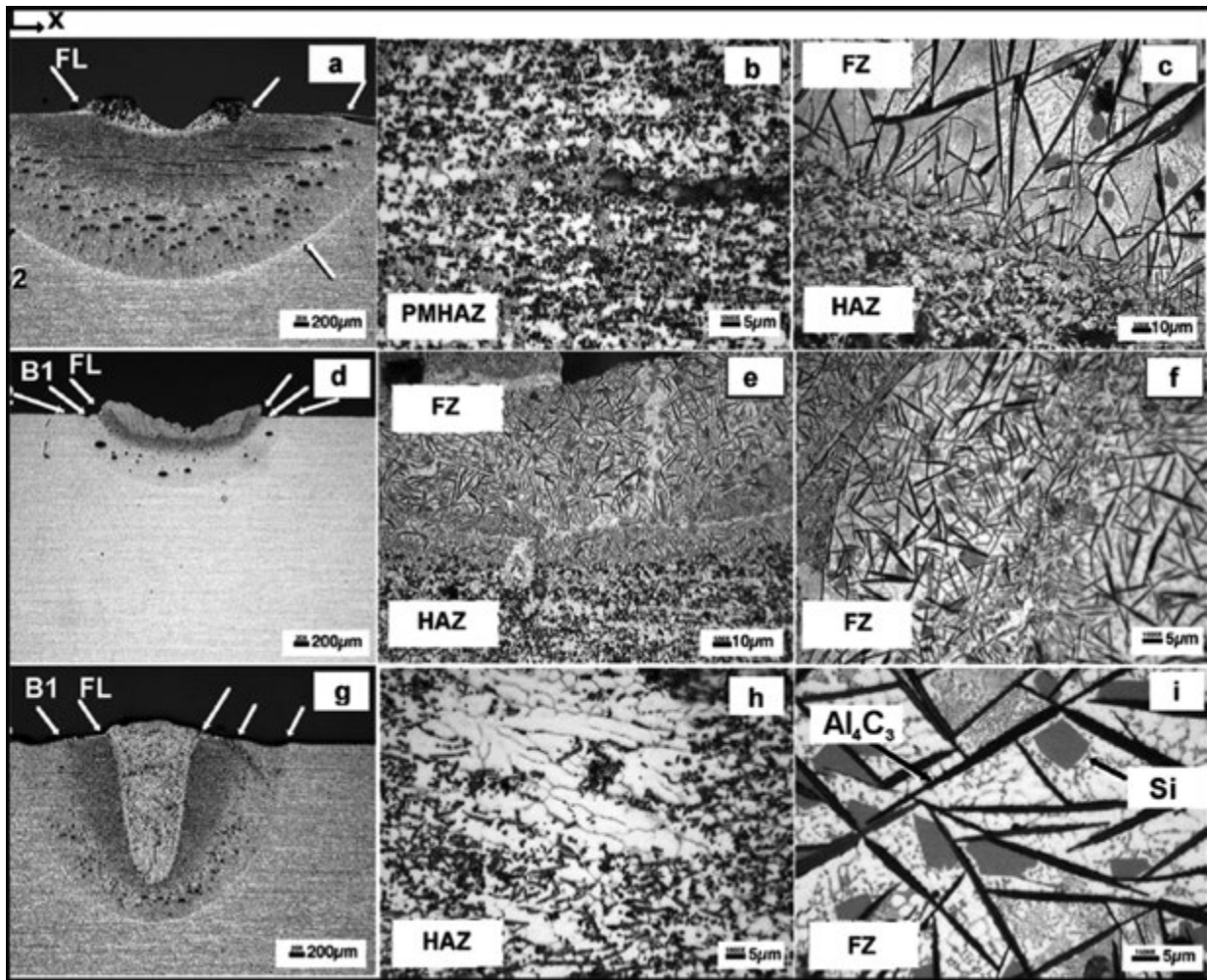


Fig. 11 Optical micrographs of fusion welds made with different welding processes on Al-SiC composites are compared: (a) through (c) the GTA welds, (d) through (f) the EB welds, and (g) through (i) the LB welds. The needle like features in (c), (f), and (i) are aluminum carbides, and the gray-colored angular precipitates are silicon phase. The fine mottled structure is eutectic constituents formed during the later stages of weld solidification. Arrows mark the approximate locations of the FL, B1, and B2. The directions x and y are in the plane of the micrographs, and the z direction perpendicular to the x-y plane is the welding direction. Reproduced from Storjohann, D., Barabash, O.M., Babu, S.S., David, S.A., Sklad, P.S., Bloom, E.E., 2005. Fusion and friction stir welding of aluminum-metal-matrix composites. *Metallurgical and Materials Transactions A* 36, 3237.

Table 3 Process parameters of EB welding of TiB₂/ZL101 MMC

Weld no.	Accelerating voltage/kV	Beam current/mA	Welding speed/ (mm/S)	Scanning frequency/Hz	Heat input/ (J/min)	Depth-to-width ratio
1	60	28	20	—	84	3.05
2	60	35	20	—	105	2.90
3	60	39	20	—	117	2.75
4	60	47	20	—	141	2.51
5	60	39	20	600	117	3.68
6	60	39	20	600	117	3.30

Note: Kun, P., Hai-chao, C., Feng-gui, L., *et al.*, 2011. Mechanical properties and wear resistance of aluminum composite welded by electron beam. *Transactions of Nonferrous Metals Society of China* 21, 1925–1931.

mechanical properties, as well as the joining technique being easily automated. The sub-melting temperatures and short weld times of friction welding allow many combinations of work metals to be joined. Filler metal, flux and shielding gas are not required in this process. Friction welding was successfully applied in case of a metal matrix composite (MMC) containing short fibers or oxide particles as the strengthening phase (Hascalik and Orhan, 2007).

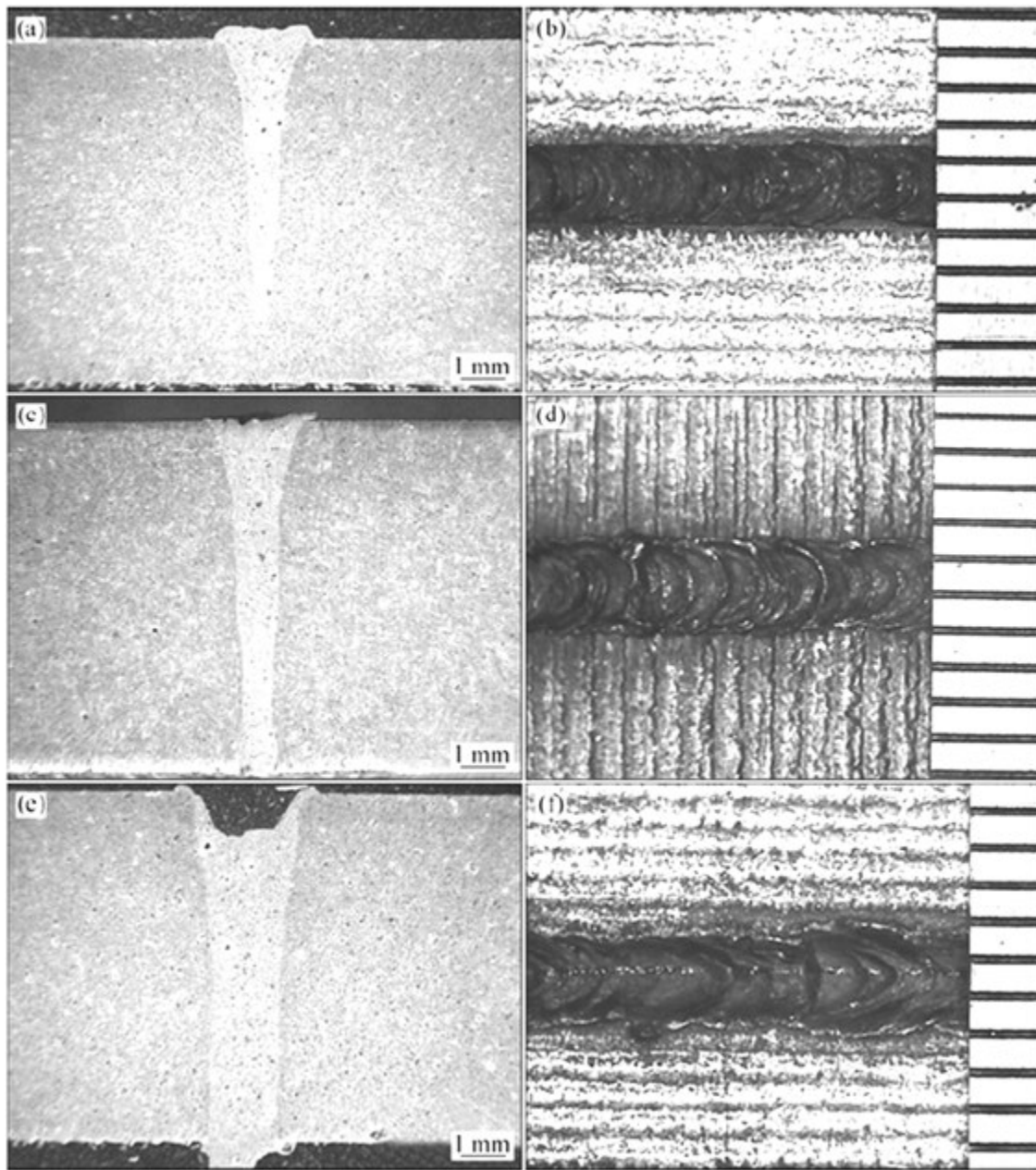


Fig. 12 Cross-section and surface appearance of welding seams of $\text{TiB}_2/\text{ZL101}$ composite under different EB process parameters: (a) and (b) 28 A; (c) and (d) 39 A; (e) and (f) 47 A. Reproduced from Huang, R.Y., Chen, S.C., Huang, J.C., 2001. Electron and laser beam welding of high strain rate superplastic Al-6061/SiC composites. *Metallurgical and Materials Transactions A* 32, 2575.

The sequential stages of friction welding process are, namely: stage I where heat is generated by sliding friction and the torque reaches its maximum value; stage II where heat is generated by mechanical dissipation in the plasticized material and softened material flows radially outwards; stage III where a steady-state situation is attained and the torque, temperature distribution and rate of axial shortening are essentially constant; stage IV where the rotation is terminated and stage V where upsetting occurs (Zhou *et al.*, 1997). Khan and Rajakumar (2018) reported that the MMCs undergo several processing such as forming and joining before turning into a usable product. Friction time, friction pressure, forging time, forging pressure, and rotational speed are the most important parameters in the friction welding method.

Hascalik and Orhan (2007) investigated the feasibility of joining Al_2O_3 reinforced Al alloy composite to SAE 1020 steel by rotational friction welding. Results indicated that Al/ Al_2O_3 composite could be joined to SAE 1020 steel by friction welding. However, it was pointed out that the quality of the joint was affected negatively with the increase in particle size and volume percentage of the oxide particles in the MMC. Sreenivasan *et al.* (2019) studied the friction welding of aluminum metal matrix composite AA7075–10 vol% SiC-T6. A continuous drive friction welding machine with 200 kN

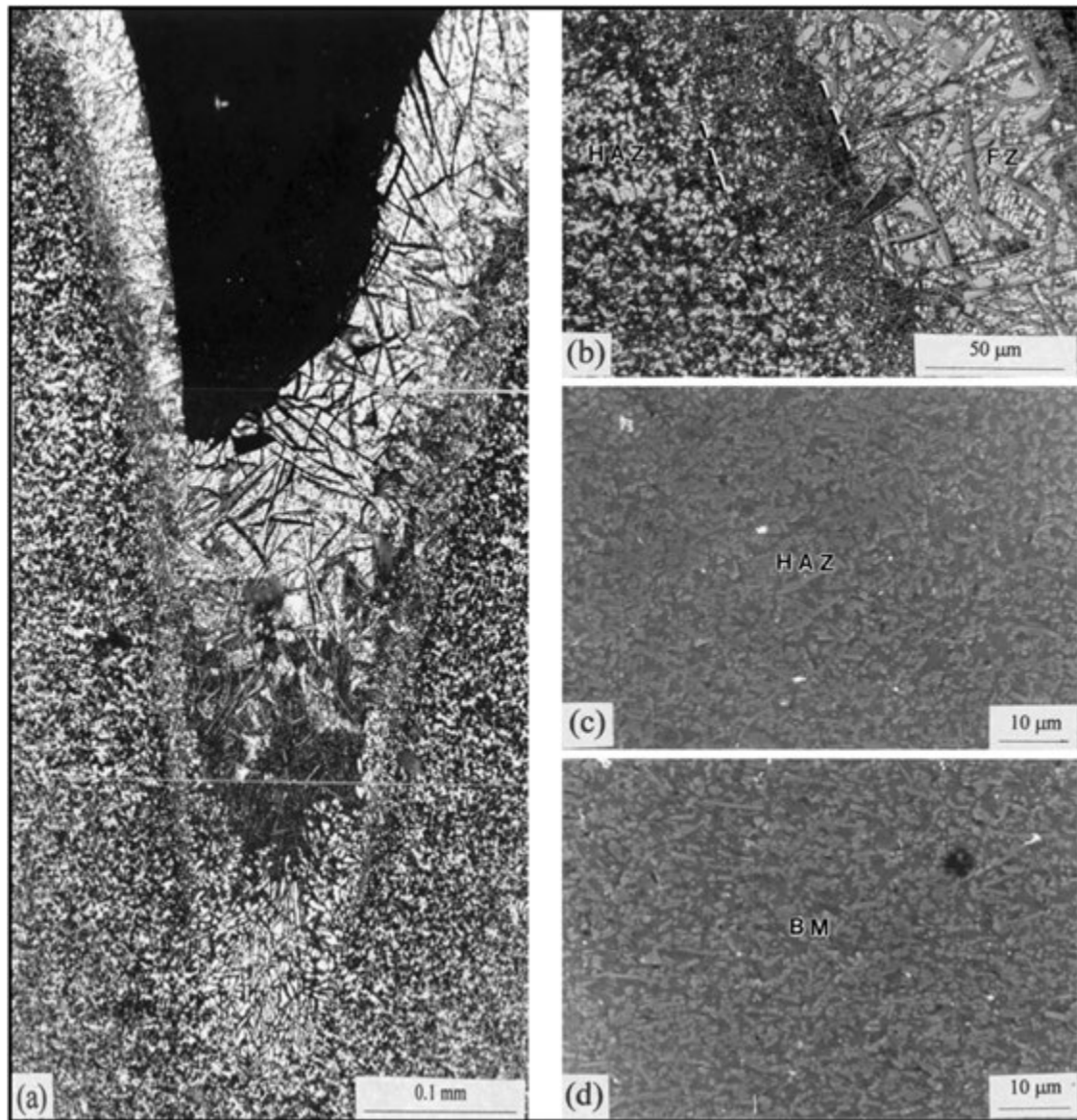


Fig. 13 Enlarged OM micrographs showing (a) the extensive Al_4C_3 reaction products in FZ and (b) the extended fusion line between the FZ and HAZ. SEM micrographs showing the SiC dispersions in (c) HAZ and (d) BM in the EB welded 6061/20 pct SiC. Reproduced from Huang, R.Y., Chen, S.C., Huang, J.C., 2001. Electron and laser beam welding of high strain rate superplastic Al-6061/SiC composites. *Metallurgical and Materials Transactions A* 32, 2575.

maximum upset force with a stroke of 300 mm and spindle speed between 1 and 2500 rpm was employed to accomplish the welding process. The most influencing process parameters in the case of friction welding are friction pressure, upset pressure, spindle speed, and burn off length. The optimized process parameter values of Spindle Speed = 1491.54 rpm, Friction Pressure = 98.94 MPa, Upset Pressure = 209.26 MPa, Burn Off Length = 1.5 mm were resulted to give ultimate tensile strength of 244.2866 MPa and hardness of 148.2392 Hv.

Khan and Rajakumar (2018) investigated on the rotary friction welded aluminum matrix composites LM25 with 10% SiC. The effect of the process parameter i.e., spindle rotation speed on the mechanical and microstructural characteristics was analyzed and studied. The microstructural examination and mechanical properties were increased with the increase in rotational speed and also aids in achieving finer microstructure. Al/ B_4C MMCs were successfully welded by the friction welding technique (Orhan, 2015). The microstructural analyzes and mechanical test revealed that welding properties were strongly affected by rotational speed and friction time. The optimal joint performance was attained at a rotational speed of 1000 rpm, friction time of 7 s, and friction pressure of 5 MPa. Nimal *et al.* (2019) investigated the friction welding of composite rods of 20 mm diameter and 95 mm length with various speeds and the micro structure and mechanical behavior are studied at the weld zone. The tensile strength and

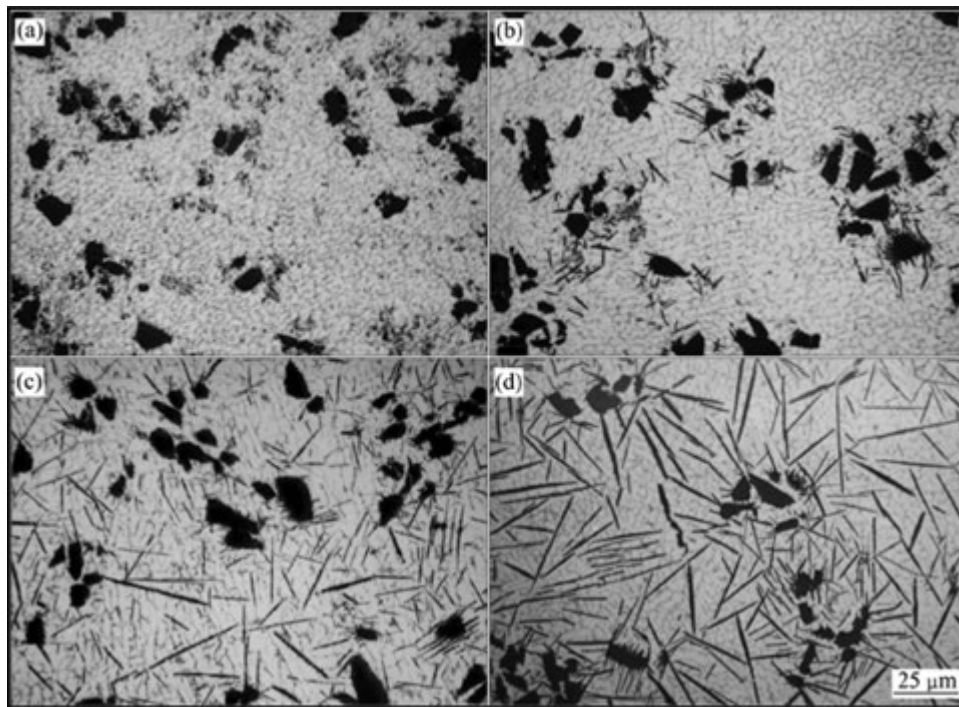


Fig. 14 Typical microstructures of EB weld in SiC_p/LD2 made at different heat inputs: (a) 30 J/mm; (b) 36 J/mm; (c) 42 J/mm; (d) 48 J/mm. Reproduced from Chen, M.-A., Wu, C.-S., Zou, Z.-D., 2006. Electron beam welding of SiC/LD2 composite. *Transaction of Nonferrous Metals Society of China* 16, 818–823.

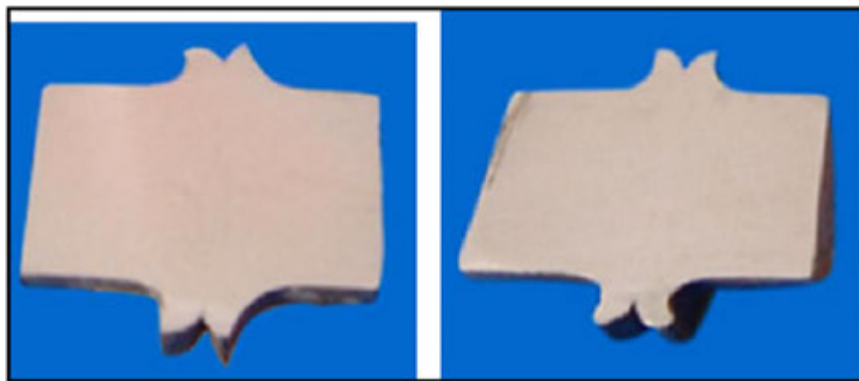


Fig. 15 Macrograph of friction welded AZ31B magnesium-Al₂O₃-Ca composite samples. Reproduced from Srinivasan, M., Loganathan, C., Balasubramanian, V., Nguyen, Q.B., Gupta, M., Narayanasamy, R., 2011. Feasibility of joining AZ31B magnesium metal matrix composite by friction welding. *Materials and Design* 32, 1672–1676.

hardness at the weld spot are high at the rod welded at 2000 rpm speed. Adalarasan and Shanmuga Sundaram (2015) and Srinivasan *et al.* (2011) reported that the optimal parameter combination predicted by the TGRA approach of frictional pressure-60 MPa, upset pressure 100 MPa, burn off length-2 mm and rotational speed-1500 rpm significantly improved the quality characteristics of Al6061/SiC_p friction welded joint.

Fig. 15 shows the macrograph of AZ31B magnesium Al₂O₃ and calcium (Ca) nanocomposite joints by rotational friction welding. Visual examination of the welded specimens showed uniform weld cross section. The flash obtained was symmetric, which indicates plastic deformation on both the rotating and the upsetting side (Srinivasan *et al.*, 2011).

The friction welding of Ti-6Al-4V matrix reinforced by 10 vol% TiC, was investigated by Da Silva *et al.* (2004) with a hydraulically driven 50 kW, 40 kN axial load at speeds up to 8000 rpm. Macrostructural evaluation as shown in Fig. 16 revealed three distinct zones such as base material (BM), heat affected zone (HAZ) and transformed and recrystallized zone (TRZ). It was

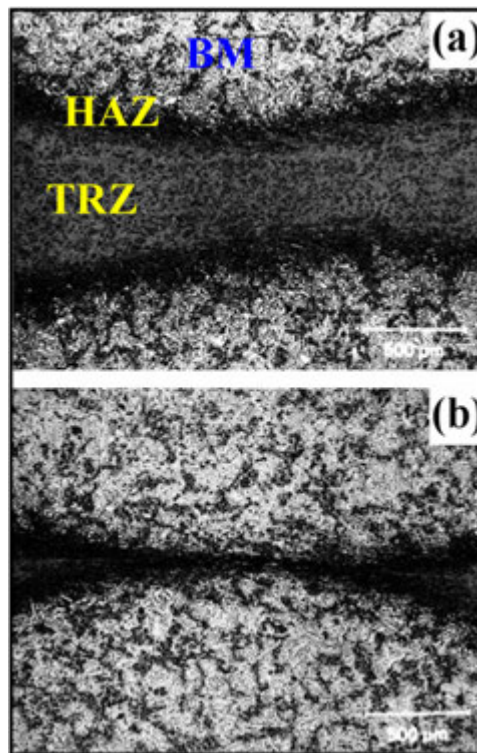


Fig. 16 Macrostructure of friction welded Ti-6Al-4V/TiC composite: (a) Condition DM 11 (1500 rpm/136 MPa); (b) DM 14 (1500 rpm/272 MPa). Reproduced from Da Silva, A.A.M., Meyer, A., dos Santos, J.F., Kwietniewski, C.E.F., Strohaecker, T.R., 2004. Mechanical and metallurgical properties of friction-welded TiC particulate reinforced Ti-6Al-4V. *Composites Science and Technology* 64, 1495–1501.

observed that both rotational speed and friction pressure influenced the weld region geometry. The forging pressure also has an influence on the size of the zones; however, it was held constant while friction welding the composite.

Park *et al.* (2011) reported the comparative studies on the relationship between the welding parameters and joining efficiency in the friction welding of hybrid Al_2O_3 -reinforced aluminum composites. The effects of the rotation speed on the reduction rate of particle size are greater than those of the upset pressure, and the area of the MMC welded zone decreases as the joining efficiency increases. During the macro-examination of the bonding interface, a gray discolored region was observed on the bonding interface, and the center of the region was dark gray. Fig. 17 shows the SEM images of the base metal and the microstructure of the weld zone at different rotation speeds.

Friction Stir Welding

Friction stir welding (FSW) is a relatively new solid-state joining process and has been developed over the past decade to join high strength aluminum alloys (Chen *et al.*, 2009). In FSW, a rotating pin tool is inserted into the edges of the work pieces and traverses along the line of the joint. The FSW process is shown schematically in Fig. 18. By friction, the rotating tool produces the heat that softens the material in the joint proximity. As the pin advances in the welding direction, the plasticized material moves from the front to the back of the pin. As a result, the joint is produced in the solid state. Due to this feature, FSW has emerged as a promising technique for joining MMCs. In particular, no chemical reaction between matrix and ceramic particles was found. However, it was reported that material stirring by the welding tool has a substantial influence on the reinforcement particles size and shape and also on their distribution in the weld zone.

Initially FSW technique was commercially used for joining Al alloys in several industries like ship building, high speed train manufacturing, welding of fuel tanks in aerospace industries, etc. It has great potential for welding of Mg, Cu, Ti, Al alloy matrix composites, lead, steel, etc (Çam, 2011). The industrial applications of MMCs were limited due to the difficulty associated with conventional welding methods, since they produced particle segregation, deleterious reactions between the reinforcement particles and liquid aluminum in the fusion zone (Marzoli *et al.*, 2006). The non-uniform microstructures were obtained when laser beam welding or arc welding (GTAW, GMAW) etc., were used. But, a solid-state welding (FSW) process has the potential to produce strong joints of MMCs with strength comparable to those of the parent material. Tool design also played an important role in FSW process. However, cost effective stirring tools were needed for welding of MMCs. Uzun (2007) fabricated a TiAlN-coated HSS-steel

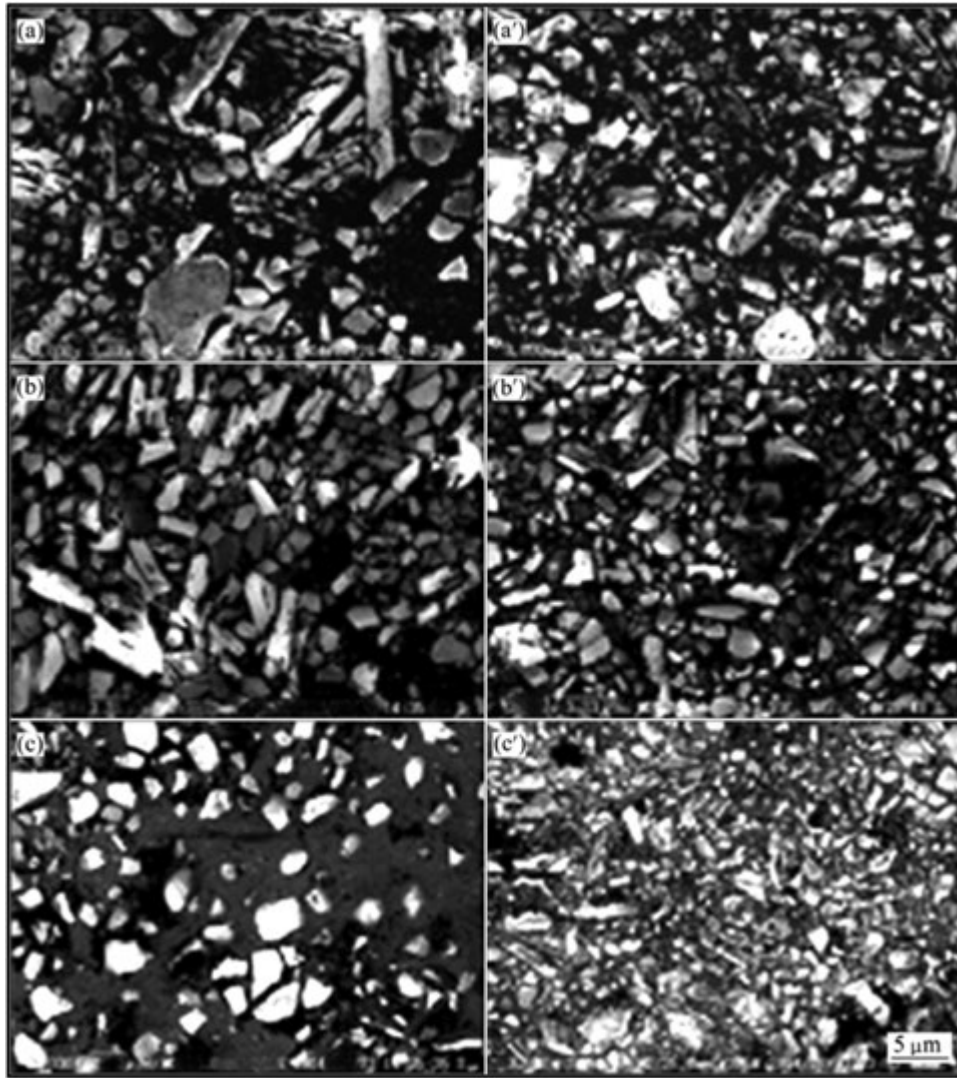


Fig. 17 SEM images of matrix (a, b, c) and welding zone (a', b', c') with different rotation speeds ($p_1=31.8$ MPa, $u_1=1$ mm, $p_2=63.6$ MPa, $t_2=10$ s): (a), (a') $n=2\,000$ r/min; (b), (b') $n=3\,000$ r/min; (c), (c') $n=4\,000$ r/min. Reproduced from Park, I.-D., Lee, C.-T., Kim, H.-S., Choi, W.-J., Kang, M.-C., 2011. Structural considerations in friction welding of hybrid Al_2O_3 -reinforced aluminum composites. Transaction of Nonferrous Metals Society of China 21, S42–S46.

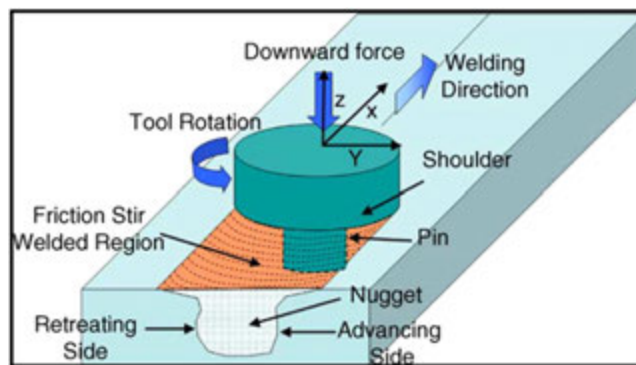


Fig. 18 Schematic drawing of friction stir welding. Reproduced from Mishra, R.S. and Ma, Z.Y., 2005. Friction stir welding and processing Materials Science and Engineering: R 50 (1–2), 1–78.

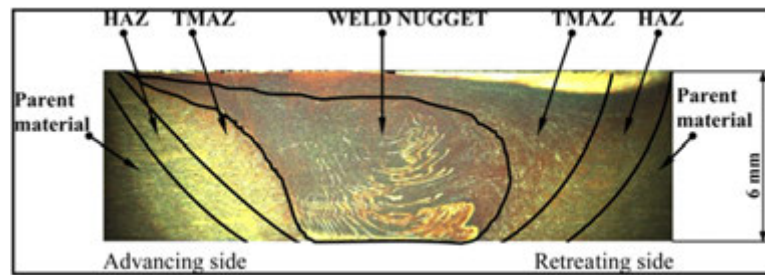


Fig. 19 Macroscopic overview of the cross-section of the friction stir welded AA2124/SiC/25p composite to itself showing typical weld zones (Weld nugget, TMAZ, HAZ). Reproduced from Uzun, H., 2007. Friction stir welding of SiC particulate reinforced AA 2124 aluminum alloy matrix composite. *Materials and Design* 28 (5), 1440–1446.

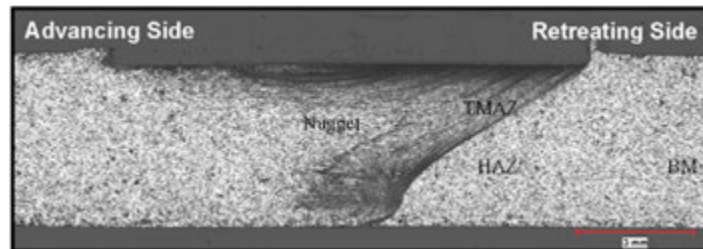


Fig. 20 Typical cross-section of FSW welds of Al-B₄C with 10.5% concentration with four distinct zones: stirred zone (Nugget), thermo-mechanically affected zone (TMAZ), heat-affected zone (HAZ) and base material (BM). Reproduced from Chen, X.-G., da Silva, M., Gougeonb, P., St-Georges, L., 2009. Microstructure and mechanical properties of friction stir welded AA6063-B₄C metal matrix composites. *Materials Science and Engineering A* 518, 174–184.

tool for joining of the AA2124/25%SiC composite having 6 mm thickness and produced the welded joint without defects. The different weld zones such as parent material, heat affected zone (HAZ), thermo-mechanically affected zone (TMAZ) and weld nugget were obtained and depicted in [Fig. 19](#).

[Vijay and Murugan \(2010\)](#) studied the effect of different tool pin profiles and welding parameters on properties of FSP zone of aluminum alloys and Al based MMC joint. The microstructures of the FS welded specimens were highly depended on the tool pin profile as well as welding speed, tool rotational speed, and axial load. It was reported that increasing the rotational speed or decreasing the traverse speed would result in a hotter weld. In order to produce a successful weld, it is necessary that the material surrounding the tool is hot enough to enable the extensive plastic flow required and minimize the forces acting on the tool. If the material is too cold then voids or other flaws may occur in the stir zone.

FSW is an important solid-state joining process that can produce sound welds with superior metallurgical and mechanical properties compared to those of fusion welding. The conventional fusion welding may produce sound joints free from defects such as voids or cracks in particle reinforced MMCs by using a low heat input during welding. But the joint properties are far below that of base metal due to the loss of reinforcement particles ([Cam and Kocak, 1998](#)). This is not valid for some particulates i.e., Al₂O₃ which is stable at weld pool temperatures. The excessive over heating during fusion welding may result in the formation of brittle phases in the fusion zone, loss of SiC reinforcement and consequent formation of Al₄C₃ ([Cam and Kocak, 1998](#)). Hence, FSW is considered to be a potential process to succeed this. Sound joints of particulate reinforced Al MMCs with up to 30 vol% ceramic particles was obtained at lower rotational and traverse speeds ([Nakata et al., 2003](#)). The range of optimum FSW conditions also became narrower with an increasing volume percentage of reinforcing particles in MMCs.

[Chen et al. \(2009\)](#) investigated the weldability of an AA6063 aluminum alloy and of two composites with A6063 matrix reinforced with 6 and 10.5 vol% B₄C using friction stir welding. A typical picture of a weld section is presented in [Fig. 20](#). It is interesting to note that, for this material, the onion rings of the stirred zone are only clearly visible on the retreating side of the weld.

[Ni et al. \(2013\)](#) achieved FSW joint of 3 mm thick SiCp/AA2009-T351 sheet using a cermet tool. [Fig. 21](#) shows the SEM microstructures of the FSW joint. In the BM, SiC particles showed a polygonal morphology and were homogeneously distributed in the matrix with the long axis parallel to the rolling direction ([Fig. 22\(a\)](#)). After FSW, the SiCp were more homogeneously distributed in the NZ. The size and aspect ratio of the SiCp were visibly decreased, and the edges and corners of the SiCp in the NZ, especially in the center and bottom of the NZ, were obviously blunted ([Fig. 22\(b\)–\(d\)](#)) compared to the sharp SiC particles in the BM.

[Uzun \(2007\)](#) presented ([Fig. 22](#)) a microstructure of welded AA2124/SiC/25p composites having different zones (1) parent material; (2) heat affected zone (HAZ); (3) thermo-mechanical affected zone (TMAZ); and (4) weld nugget. TMAZ is characterized

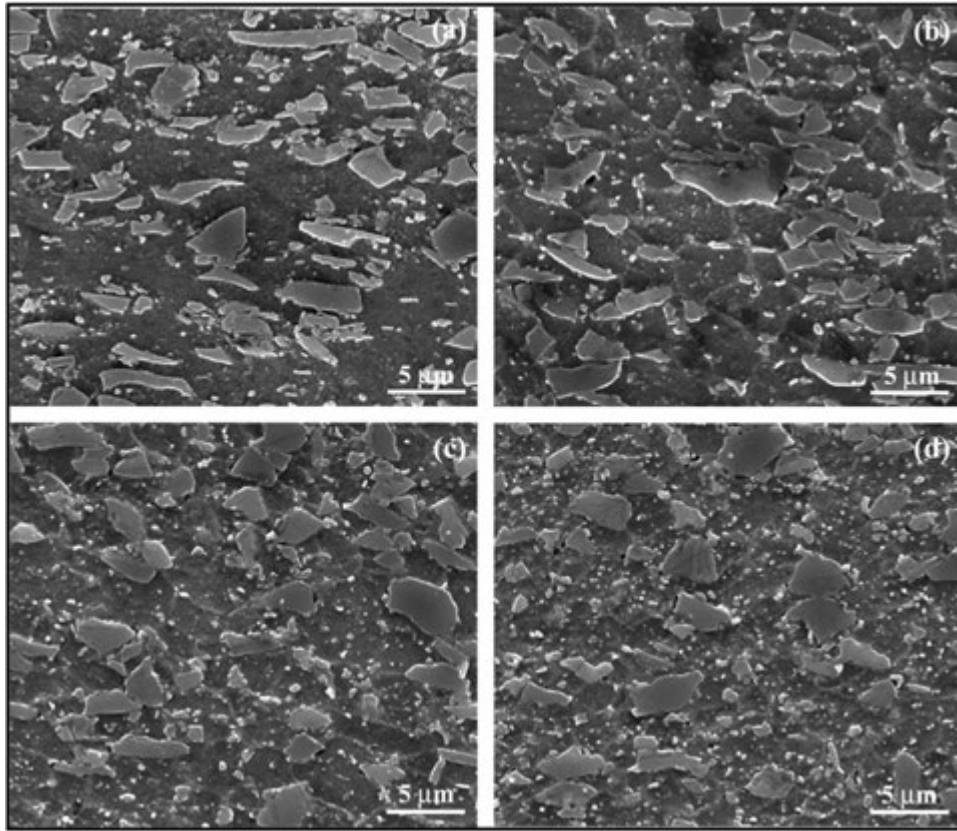


Fig. 21 SEM microstructures of FSW SiCp/AA2009 joint: (a) BM, (b) top of NZ, (c) center of NZ, and (d) bottom of NZ. Reproduced from Ni, D.R., Chen, D.L., Wang, D., Xiao, B.L., Ma, Z.Y., 2013. Influence of microstructural evolution on tensile properties of friction stir welded joint of rolled SiCp/AA2009-T351 sheet. *Materials and Design* 51, 199–205.

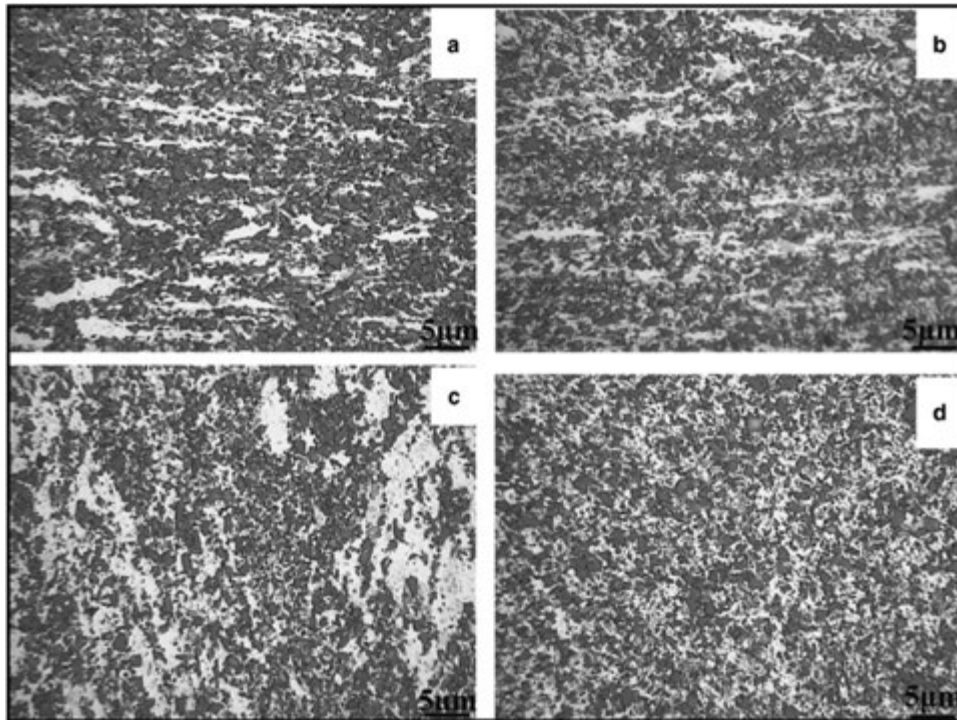


Fig. 22 Optical microstructures of the FSW joint of the AA2124/SiC composite: (a) parent material; (b) heat affected zone (HAZ); (c) thermo-mechanical affected zone (TMAZ); and (d) weld nugget. Reproduced from Uzun, H., 2007. Friction stir welding of SiC particulate reinforced AA 2124 aluminum alloy matrix composite. *Materials and Design* 28 (5), 1440–1446.

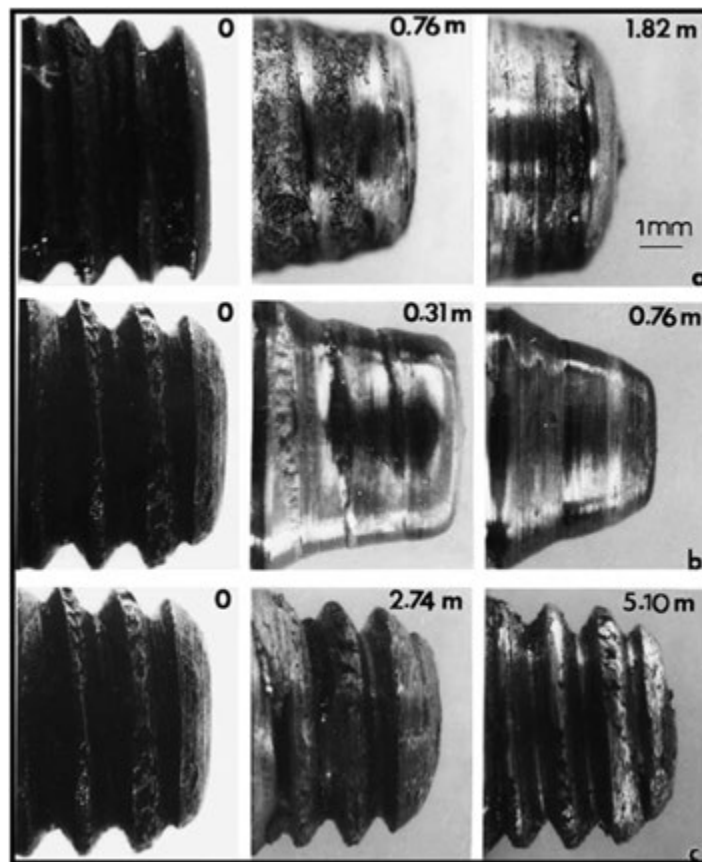


Fig. 23 Tool (nib) sequences showing FSW wear features. The corresponding locations for linear traverse are indicated in each photograph. (a) MMC FSW at 500 rpm, (b) MMC FSW at 1000 rpm, (c) 6061 aluminum alloy FSW at 1000 rpm. Reproduced from Prado, R.A., Murr, L.E., Hinds, D.J.S., Soto, K.F., 2001. Tool wear in the friction stir welding of aluminum alloy 6061 + 20% Al_2O_3 : A preliminary study. *Scripta Materialia* 45, 75–80.

by a rotation of the elongated grains of the Al alloy matrix and the SiC particle-free regions of the composite. The SiC particle alignment was also observed in the TMAZ region. The HAZ exhibit a microstructure similar to the base AA2124/SiC/25p composite.

Prado *et al.* (2001) studied the comparisons of several tool/nip image sequences corresponding to tool rotation speeds of 500 and 1000 rpm in the joining of 6061-Al-20% Al_2O_3 MMC and found no apparent tool wear for the FSW in the Al 6061. The photographs in Fig. 23(a) and (b) show a recognizable difference between FSW regimes corresponding to 500 and 1000 rpm, with greater wear in the 1000 rpm regime.

Summary and Future Outlook

This article presented an overview of joining of MMCs using various fusion and solid-state welding techniques. The microstructures of the joint zone were explored in detail and the effect of some of the process parameters were presented. Fusion welded joints failed to retain the original distribution of reinforcement particles in the parent composite. The fusion initiated unwanted reactions between the matrix material and the reinforcement to produce brittle intermetallic particles. On the other hand, solid state welding processes improved the distribution of the reinforcement particles in the joint region due to intense plastic deformation and movement of plasticized material. The solid-state nature curbed any possible deleterious interfacial reaction and a superior interfacial bonding was realized. However, the speed of such processes is low compared to that of conventional fusion processes. The abrasive action of the ceramic reinforcement particles often poses a huge threat to the life of the tool in case of FSW. An improvement in tool design and coatings are to be developed to realize successful continuous welding of MMCs with varying volume fraction of reinforcement particles. Methods to be discovered to reduce or nullify the reactions during fusion welding to take advantage of the high welding speed to increase production. MMC research is reaching another level with the advent of new generation of nano particle reinforcements which present new challenge for the weldability of composites. Advancement and modification in existing technologies are required to successfully weld nano composites.

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Emerging Technologies for In-Situ MMC Production

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Introduction

The requirement for and development of new materials for efficient utilization of any component has seen an upsurge in the research sector. The present day requirements of materials should be able to withstand large stress, heavy loads and also be operative in unforeseen climatic conditions. These requirements to be achieved with traditional materials are highly unfeasible due to the defined properties in only one criterion and hence the requirement of composite is essential. Composite in general can be stated as a mixture of two or more substances that exhibit the distinction chemically at microscopic scale, have specified boundary of distinction and can be identified conveniently. The proportions of these constituents are reasonably chosen and the exhibition of composite properties should be higher in all terms with respect to constituent properties (Surappa, 2003). The substance available in large scale and is continuous in nature is termed to be matrix and the substance that is added to enhance the property of the matrix is termed as reinforcement. The materials of certain properties that are unable to be developed by alloying or heat treatment can be easily developed by compositing. This process can be achieved by varying the type of reinforcement being used, size, distribution and shape (Withers, 2014). Among many class of composites, metal matrix composite has seen a huge advancement in research sector. Metal matrix composites are a class of composite materials that have ceramic as reinforcement and a metal or its alloy is utilized as a matrix. The fundamental principle of addition of reinforcement is to enhance the various physical, mechanical, thermal and chemical properties of the developed composite. The addition of reinforcement could be in any form from whiskers, fibers or particulates. The type of matrix material used, reinforcing agent and manufacturing techniques plays an important role in determining the various properties of the composite (Das *et al.*, 2016). Aluminum, the copious material available in earth's crust has seen its emerging significance since the medieval period and has contributed for the process of industrial revolution. The dawn of 19th century that led to successful extraction of aluminum found large scale applications in domestic and industrial sector (Nappi, 2019). Aluminum composites are the materials that are exhaustively used in numerous engineering fields. The exploration of these materials has paved the path to term this material to be superior in terms of its availability and properties, ease of processing and formation of well defined bonds between the reinforcement of various forms in comparison to other monolithic materials in existence. The sectors like aerospace and automotive have found vast scale application of aluminum composite due to its desirable properties like appreciable strength and elastic modulus, resistance to wear and low values of thermal expansion coefficient (Gupta *et al.*, 2014; Jha *et al.*, 2014).

Classification

The classification of MMC is largely dependent on numerous factors like type, shape, size, and process of incorporating the reinforcement.

Particle Reinforced MMC

The type of reinforcement is in the form of particulates. Ceramics are usually preferred as reinforcements in this form which are equal in length such as oxides, nitrides and borides. The content of reinforcement in the matrix is less than 30% and the aspect ratio is about 5. The method of preparation of these forms of composites is done by integration of matrix and reinforcement followed by solid state sintering or certain techniques of liquid process like in-situ, squeeze casting and stir casting.

Continuous Fiber Reinforcement

These form of composites are made up of materials such as Al_2O_3 , SiC or carbon which are continuous in nature having the diameter of 20 μm . These forms of processing fibers can be parallel to each other or pre woven. The other form can be of coarse fibers or monofilaments which are difficult to be made flexible for producing varied shapes of materials. Monofilaments on the other hand have a diameter of 100–150 μm that are commonly produced by chemical vapor deposition techniques.

Whiskers and Short Fiber Reinforced MMC

The kind of reinforcement used in this is not continuous and have an aspect ratio more than 5. The processing of these reinforcement is usually carried out by powder metallurgy or the process of squeeze infiltration into fiber perform. The parts produced through these are near net shape. The wide usage of this form is seen in development of piston where Al_2O_3 fiber reinforced pistons are developed. The disadvantages of these reinforcements with heat deterioration have restricted its usage to greater extent.

Hybrid MMC

The combination of one or more form of reinforcement into the matrix to usually enhance the overall properties of the composites is hybrid MMC.

Processing

The process used for development of various composites determines the desired properties to be obtained. Most of the processing methods are divided into primary processing and secondary processing techniques. The primary process involves, blending of the reinforcement and matrix and not to yield a net or near net shape of the composite. the primary processing is followed by secondary process that changes the required properties from microstructure to physicality for enhancement of physical and mechanical properties. The choice of the process to be utilized for manufacturing is dependent on the type of matrix and reinforcement and the temperature to which it should be processed into. The fundamental classification of these processing process are classified as follows:

Solid State Processing

As the name suggests these kind of processes are used for blending of reinforcement into the solid state matrix by combination of various materials that would produce a high combination of properties. The parts developed by these processes are primarily used for application that involves precision and high performance like aerospace and automotive, they also have very high fatigue strength. At the beginning the process was followed by ceramic whiskers which were later developed to use ceramic particulates. The economical implication of this process is very high for procuring the reinforcement as well as the processing. The utilization of ceramic whiskers has been taken over by particulates due to numerous health implications involved. However, above all the parts developed by this process had very high performance applications (Srivatsan *et al.*, 1991). Powder blending and consolidation and diffusion bonding are two major processes that occupy the space under solid state processing.

Liquid Metal Processing

The method involves the process of stir casting through which a reinforcement either in the form of particles or short fibers and incorporated into the molten matrix. The process of stir casting allows the principle of stirring the matrix and reinforcement at given velocity and then providing sufficient time for solidifying the composite, usually ceramic reinforcement is used in aluminum matrix. The basic criterion in this process is to have proper wettability between the reinforcement and the matrix as this plays an important character in determining the increment in desired properties. The amount of reinforcement that could be incorporated into the matrix would be up to 30% which would be in the size range of 5–100 μm that could be used in numerous forms of molten alloys (National Centre for Manufacturing Sciences, 2002). Apart from the process of stir casting, another method compo-casting is also used to develop the composite. However, the reinforcement is added in the semi solid state of matrix (Surappa, 2003). Other methods like squeeze casting, liquid infiltration, hot forming are also used for development of composites.

Vapor State Processing

This method of processing includes layup of reinforcement over the matrix in layer wise. The advantages of this method are to adopt proper bonding between the matrix and reinforcement without undergoing any untowardly reaction between the two phases.

Plasma/Spray Deposition

The method of plasma spray coating is widely used in the production industries for development of numerous protective coatings (Rätzer-Scheibe and Schulz, 2007; Helminiak *et al.*, 2009). The coatings applied to mechanical surfaces exhibit very high values of hardness along with enhanced corrosion resistance and abrasion. These properties greatly benefit the working of the machinery and enhancing the lifespan (Wang *et al.*, 2013). Metal based composites with ceramic as reinforcement is used as a material for plasma spray coating (Luo *et al.*, 2015). The combination of this matrix in metal form and ceramic in reinforcement will add to greater toughness and hardness of the coatings. The most representative metal matrix composites are usually Ni-based or Co-based alloys containing SiC, TiC, WC, La_2O_3 , or Cr_3C_2 (Zhou and Dai, 2010; Yin *et al.*, 2010; Huang *et al.*, 2015).

In-Situ Processing

Certain processing techniques like diffusion bonding, powder metallurgy, stir casting, squeeze casting and spray deposition the process of development of composites is carried by the method of ex-situ in which the reinforcing agents are prepared separately and added to the matrix. This kind of manufacturing process involves poor interfacial interaction between the matrix and

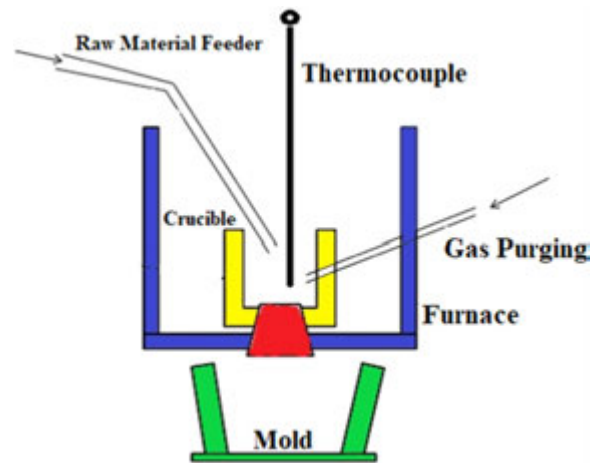


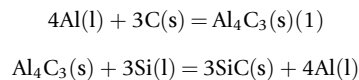
Fig. 1 Schematic of the exothermic dispersion process.

reinforcement, the wettability of these reinforcements is not done properly and also the variable size of reinforcements is not common which depends on the initial size condition of the powder (Tjong and Ma, 2000). To overcome the problems of these forms a new method known as in-situ technique is used for development of MMCs. The effect if certain chemical reaction in the metal matrix leads to the formation of reinforcement which provides numerous advantages like thermal stability of the reinforcement in the matrix, sturdy interfacial bonding is seen between the matrix and reinforcement due to no impurities found in the process, reinforcing particle size of any size and shape are distributed evenly in the metal matrix which leads to enhancement of mechanical properties and this method of production is more cost effective than ex-situ (Gnjidic *et al.*, 2001; Merzhanov, 1995). The process of in-situ reinforcement is carried out by certain methods such as self-propagating high temperature synthesis (SHS) (Sheibani and Najafabadi, 2007), exothermic dispersion (XD) (Kuruvill *et al.*, 1990), flux assisted synthesis (FAS) (Laksmi *et al.*, 1998), direct metal oxidation (DIMOX), mechanical alloying (MA) and reactive hot pressing (RHP) (Tjong and Ma, 2000).

Exothermic Dispersion (XD)

This method of in-situ process allows dispersion of ceramic reinforcement in Al matrix to build a composite. Initially the process is begun by developing mixtures of powder of the required constituents, converted to pellets and the fed into the melt with continuous stirring. The process of exothermic dispersion is shown in Fig. 1. Stirring is used to disperse the reinforcement in an evenly manner. Oxidation reaction in the melt is prevented by purging inert gas like nitrogen into the melt. The crumple of bubble formed in cavitations releases large amount of energy which leads to consistent dispersion of reinforcement. However the properties such as porosity, formation of clusters of particles and agglomeration will directly impact the mechanical properties of the composite. Addition of numerous reinforcements helps in enhancement of yield strength, tensile strength and elastic modulus. SiC particle reinforcement facilitates improvements in these properties and has an effect on ductility reduction.

Introducing of SiC has been tried in numerous forms such as SiC in untreated form, by milling Al-SiC particulate and Al-SiC-Mg composite powder (Amirkhanlou and Niroumand, 2011). The direct usage of untreated SiC affects in formation of agglomerates and uneven distribution. However, the usage of Al-SiC-Mg composite powder helps in proper wettability of SiC through Mg and also helps in improvising the interfacial bonding. In a way composite powders helps in appropriate distribution of SiC into the melt and also improves distribution. The adaptation of in-situ composites to have certain desired properties is achieved by variation of temperature which leads to restrain the formation of intermetallic phases by Si and C components. The composite with SiC as reinforcement prepared at 950°C is devoid of Al₄C₃ phase however, this is seen in the brittle from when developed at 750°C. At elevated temperatures the reaction of Al₄C₃ is evident and free form of Si in the process of in-situ undergoes dispersion in the matrix (Du *et al.*, 2014a,b). The reaction that undergoes in this formation is as follows



Self Propagating High Temperature Synthesis (SHS)

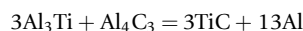
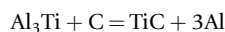
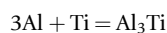
The process of SHS involves the facilitation of reactions by igniting the elements which in turn carries the required energy by certain chemical reactions and converting them to thermal energy. After the sufficient temperature is attained the process becomes self sustained and the heat energy propagates through progression of enthalpy in the fore front of the reactions. The mechanism involved in SHS is rapid and which accommodates quick heating and cooling resulting in quenching which makes the process feasible to have its impact at nano scale as well. Numerous researches have been carried out in SHS, Li *et al.* (2007)

Table 1 Reactants of wet and dry milling

Reaction	Milling speed	Milling conditions	Phases present after	
			1 h	10 h
$3\text{CuO} + \text{Al} \rightarrow 3\text{Cu} + \text{Al}_2\text{O}_3$	300 rpm	Dry milling Wet milling	$\text{Cu} + \text{Al}_2\text{O}_3 + \text{Cu}_9\text{Al}_4$ $\text{CuO} + \text{Al}$	$\text{Cu} + \text{Al}_2\text{O}_3 + \text{Cu}_9\text{Al}_4$ $\text{CuO} + \text{Al}$

Note: Das, D., Samntha, A., Chattopadhyay, P.P., 2006. Development of bulk nano- Al_2O_3 dispersed Cu-matrix composite using ball milled precursor. In: Proceedings of the International Conference on Advances in Materials and Materials Processing (ICAMMP). India: IIT-Kharagpur.

have developed Al–TiC composite by the method of SHS by using laser as ignition method. Al_3Ti formation that results in the reaction process is controlled by unstabilizing the molar content ratio of C–Ti. The presence of Al_3Ti that could be overcome by carrying out the process at proper melt temperature and variation of C–Ti ratio. Temperature plays an important role in determining the presence of Al_3Ti , as the temperature is increased the reaction between the C and Al_3Ti enhances and TiC precipitates as final product. The enhanced content of C in the matrix may arise to the reaction with Al to form Al_4C_3 , however, as the temperature increases the thermal instability of Al_3Ti and Al_4C_3 increases and leads to formation of TiC particles. The following reactions may be noted in the process of SHS which leads to formation of TiC.



Mechanical Alloying (MA)

This method of development of composites involves utilization of mechanical energy and converting the same to stimulate the chemical reaction and also implement the structural changes. This is also called as mechanochemistry or mechanochemical synthesis as well (Suryanarayana, 2001; Zhang, 2004). In the recent times, high energy ball milling (HEBM) or Mechanical Alloying (MA) which induces the reduction reaction in aluminum matrix is gaining large scale importance due to the ability to synthesis the micro and nano scale reinforcements in MMCs (Matteazzi and Le Caer, 1992; Zhang, 2004). The process involved in HEBM is unique which creates a reaction mechanism that produces the metastable material by mechanical activation which is difficult to be produced by conventional methods (Shingu and Ishihara, 1995). The production of materials is in the form of nanocrystalline which enables them to showcase efficient properties and performance in comparison to their counter parts which are coarse grained in nature. Powder particles undergo continuous and repetitive cycle of fracturing, welding and re-welding in the process of MA (Prabhu *et al.*, 2006). The methodology of MA involves the preparation of powder blend in the bowels called vials, in which the required quantity of powder is grinded in the suitable medium. The time interval in which this process is carried out is dependent on the required composition where the size of the particles will be in proportion with comparison to initial powder mix. The major apparatus involved in this process are the raw materials and the devices compatible for milling, either planetary mills or vibratory mills are being used for the process. The initiation of chemical reaction takes place by through shearing action or high impact force being led by balls over the powder (Suryanarayana, 2001; Murthy and Ranganathan, 1998). The mechanics of chemical reaction is dependent on the transfer of mechanical energy which in turn is dependent on various parameters of milling such as milling type and speed, ratio of ball to powder, dry or wet milling and the duration of process. Numerous researchers have carried out the analysis of MA process. Lu and Zhang (1999) have analyzed that in the matrix of Al–Mg system the process of milling will drastically influence the reaction in the existence of process control agent (PCA). The utilization of PCA for milling of Al and Mg powders for a period of 5 h has resulted in the formation of Al_3Mg_2 . It was observed that the presence of PCA will have a greater effect on the generation of new compound. However, the kinetics of reaction is solely improves with minimal amount of PCA. In another study by Das *et al.* (2006) the study was conducted to analyze the effects of reaction for $\text{CuO} + \text{Al}$ system in which Al_2O_3 was used as a reinforcement agent. Comparative study was done by inculcating the process of analyzing the reactions by both wet milling and dry milling. Toluene was used as process control agent in wet milling and the reactions were analyzed. The study has revealed that the presence of toluene has hampered the mechanosynthesis reaction between CuO and Al . The duration extension of the reaction has not deterred the kinetics of the reaction. When the results were observed in the process of dry milling the reaction had led to results in 1 h of the process. The study helps in understanding the effects of utilization of PCA in the mechano–chemical reaction. Table 1 indicates the reaction analysis of these two processes.

Additive Manufacturing

The development of composite materials through conventional methods has its own hindrances such as longer time for manufacturing, utilization of larger energy for development, uncontrolled agglomeration, large grain structure and many more (Banerjee

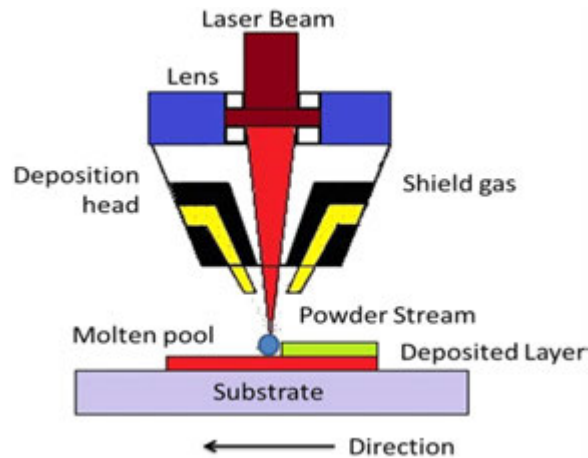


Fig. 2 Working principle of the LD-AM process.

et al., 2003). With these problems there arises the need to develop a process that exhibits efficient performance, cost effective and is controllable in the process of manufacturing. Laser Additive Manufacturing (LAM) is one such advanced and emerging technology in manufacturing that enables to develop metallic components that overcomes the above uncertainties. Numerous researches have been carried out in development of Ti based materials using the process of LAM (Attar *et al.*, 2015; Liu and DuPont, 2003; Hu *et al.*, 2016). There are many noted process of LAM such as selective laser sintering and selective laser melting which are less efficient than laser deposition additive manufacturing process. The ability of development of parts, including remanufacturing, minimal heat zone area for high energy parts and easy fabrication of functional materials (Ning *et al.*, 2016; Gu *et al.*, 2012; Ning and Cong, 2016; Li *et al.*, 2017). Hu *et al.* (2017) have experimented the development TiB reinforced composites by the process of LDAM (Laser Deposition Additive Manufacturing). The process of manufacturing was carried out by using laser engineered net shaping machine. The procedure of development of parts using this process is illustrated in Fig. 2. The emission of laser over the specified area creates the molten pool over the surface of the specimen. The energy of the beam develops greater molten area which provides the space for accumulation of powder through the feeder. As the utilization of laser beam ceases the solidification of molten area is seen to begin rapidly due to fast dissipation of heat. The developed 3D file navigates the path of deposition head in the designated trajectory which eventually develops the first layer. The deposition head is further set to required position after the completion of first layer. The ascending position is treated to be of one layer thickness. With the formation of second layer, melt is seen over the first layer during the deposition. The whole part is developed in this manner. Banerjee *et al.* (2002) have developed TiB reinforced composites and have observed homogenous dispersion of Ti in the matrix. In another experiment Dutta *et al.*, have manufactured TiB composites by using it as a protective layer over Ti₆Al₄V substrate by using Ti and B powder melt developed by the process of LD-AM (Dutta Majumdar and Li, 2010).

Applications and Challenges

Design of in-situ composites by rightfully balancing the properties through varying the content of constituting phases is very important to meet the requirements of any applications. Depending upon the requirements of any engineering component or part, the development of in-situ composites are composed of simple metal like aluminum to complex materials like ternary transition metal silicides as matrix materials and ceramic based materials as reinforcements. Currently, many metal matrix composites developed via ex-situ techniques are being used for building various automotive and aerospace structures. Feasibility studies are being carried out to explore the possibility of replacing ex-situ composites by newly developed in-situ counterparts due to their number of advantages. Recent development in the area of in-situ composites for possible structural and non-structural applications is presented in this section. Owing to their promising physical and mechanical properties the in-situ composites can be used for durable and stable structures.

Automotive industry is currently using iron and aluminum alloy based engine components which are turning out to be expensive from fuel consumption and maintenance point of view. The stress is on employing light-weight materials which not only reduce the weight of a component or overall structure but also better in performance when compared with existing materials. In this regard, Al-Si based in-situ composites are being developed by many reputed institute and national research labs like Council of Scientific and Industrial Research, India. Al-Si alloys like A356 and A390 were reinforced with in-situ developed materials like Mg₂Si and primary silicon particles for possible applications like automotive pistons and cylinder block liners (Ram *et al.*, 2017; Arsha *et al.*, 2015). The tensile properties at elevated temperature ranging from 150°C to 300°C were studied and peak value of 178 MPa obtained at testing temperature of 150°C. The study was intended to develop better and improved in-situ composite which can overcome the softening of Al-Si alloy at elevated temperatures in cylinder block liner application. Many companies are also working on in-situ composite based engine components like connecting rods. Advanced Materials Technology,

Germany has developed titanium based composite in which titanium boride is formed via in-situ process. The tensile strength at room and elevated temperatures (600°C) were 1320 and 810 MPa, respectively. The elastic modulus was found to be 136 and 81 GPa respectively at room temperature and 600°C (AMT, 2014). One can observe that this in-situ composite has high stiffness and strength at elevated temperatures which is quite for compressor blades, transmission shifts and landing gear applications. In case of aerospace industry or power plants the gas turbines are used for power generation and need to have components that can sustain high temperatures. With increasing requirements the gas turbine engines are experiencing very high temperatures exceeding the melting temperatures of blade or airfoils material. In such cases the need for better engine performance and efficiency has triggered lot of research work and development of new materials (Bewlay *et al.*, 2002). United States based General Electric (GE) and Russian based All Russian Scientific Research Institute of Aviation Materials (VIAM) companies are actively working on niobium based in-situ composites owing to their high thermodynamic stability (1350°C) which is comparatively higher than that of currently used heat resistant nickel alloys (HRNA) for the development of casting blades in gas turbine engine applications (Kablova *et al.*, 2017). Apart from high temperature applications, there is also need for new advanced materials for ship and offshore industries for low temperature applications. In this regard novel material like Al/Al₂O₃ in-situ composites are developed to cater the need of thermal stabilization of superconducting wires. The in-situ composite with 1.93% Al₂O₃ content showed a relatively high strength over 400 MPa at a low temperature of 77K which is suitable for mechanical stabilization of superconducting cables (Kovac *et al.*, 2017).

Applications in which primary importance is not mechanical but electrical, thermal or surface protection are known to be non-structural. Advanced power generation plants and gas turbines need to perform under hostile environments composed of wear and corrosion. Especially the turbine blades which operate in the hottest section of the engine, the blade material faces very high temperatures close to 1300°C and highly corrosive environments composed of NaCl, V₂O₅, and Na₂SO₄ like contaminants. For such cases the materials need to have high hardness, anomalous hardness-temperature dependence good wear and corrosion resistance. Novel Co₃Mo₂Si/Co in-situ composite coating was developed by laser cladding technique to protect the turbine components (Liu and Wang, 2010). Presence of hard intermetallic compound Co₃Mo₂Si was found to be capable of enhancing hardness of in-situ composite as large as 690 HV. In addition to this, the in-situ composite was found to be insensitive to wear load and the wear loss curve was almost flat. On the other hand Ti₆Al₄V–TiB in-situ composite coatings were developed using laser metal deposition technique aiming at high corrosion and wear resistance for medical implants (Popoola *et al.*, 2016). The need for such composite coating was based on the studies which have shown that traditional Ti₆Al₄V alloy possess poor wear and corrosion resistance. Due to laser cladding and presence of in-situ formed TiB, the coatings showed reduction in the toxic effect emanating from aluminum and vanadium ion release. Materials with low coefficient of thermal expansion are attractive materials for packaging electronic applications. Conventional materials do not fulfill the needs of present day applications and need modifications in their composition or all together development of new material. Take for example Si–Al alloys suffers from non-uniformity in the size of primary silicon particles. For such case the Si–Al alloy was reinforced with in-situ developed TiB₂ particles which not only refined primary silicon but also enhanced the thermal conductivity (84 W/mK) and lowered the thermal expansion coefficient ($6.6 \times 10^{-6}/\text{K}$) making them ideal for electronic packaging applications (Zhang *et al.*, 2012). All these works have shown that the conventional ex-situ composites and different metallic alloys can be replaced with appropriate in-situ composites for better performance in their respective structural and non-structural applications.

The advantages of in-situ composites might be more than that of ex-situ counterparts but they do suffer from certain drawbacks related to processing, composition, defects introduction and obtaining in right of set properties for certain material combinations. It is well known that the in-situ reinforcements during the processing are synthesized via precipitation process by facilitating reaction between different constituents. But the choice of developing reinforcement is limited to those which are thermodynamically stable within that particular matrix material. In such case one cannot develop all of types of reinforcements in one specific metal or alloy. Take for example, TiC is known for its high melting point and hardness next to that of diamond. But its synthesis requirements are quite harsh as its synthesis temperature is close to that of 1700°C and require long reaction time of over 10 h. If carbothermal reduction method is adopted for synthesis of TiC then one can find that there is poor reaction between C and Ti due to limited mass transfer conditions of solid to solid reactions. If direct carbonization technique is used for synthesis of TiC then one needs to have very fine size of C and Ti powders. This is because if the starting powders chosen are of coarse size than the reaction might need 5–20 h and reaction is difficult to control (Wei *et al.*, 2011; Lee and Thadhani, 1997). On the other hand obtaining uniform size and shape of reinforcing phase is quite cumbersome job during processing stage. Since kinetics of the system largely defines the size and shape of reinforcing phase significant flexibility might not be available to control the same. Synthesis of TiN particles using selective laser sintering is largely dependent on the laser energy density. At low laser energy density (2.5 kJ/m) the TiN phase obtained had non-uniform angular structure with large size and found to have certain degree of clustering. On the contrary at higher laser energy density (5 kJ/m) the TiN had granular morphology with small size and homogeneous dispersion of matrix (Gu, 2015).

During processing the chemical reactions take place between precursors leading to the formation of reinforcing phases in the matrix material. However there are certain phase transformations which are undesirable from mechanical or physical properties point of view. Take example of Al–Ti system which is necessary for the synthesis of Al–Al₃Ti in-situ composites either by powder or liquid metallurgy route. Al₃Ti particles which are known to be most thermodynamically stable phase are formed due to reactive diffusion between Al and Ti. During Ti to Al₃Ti phase transformation large volume expansion is introduced due to which micro-cracks are nucleated in the Al₃Ti particles. The formation of micro-cracks results in particle during application of external load leading to poor mechanical properties (Zhang *et al.*, 2011). In addition to this due to Kirkendall's effect the vacancies are generated

in aluminum which with respect to time tends to coalesce and form noticeable voids and porosities in the composites thereby affecting the relative density. Similar to this aluminum alloys containing copper as major alloying element shows the formation of brittle intermetallic compound CuAl_2 . Presence of such compound in eutectic structure makes the in-situ composite sensitive to brittleness resulting in lowering of mechanical properties. The processing temperature also plays an important role in defining the microstructure and mechanical properties. In case of the $\text{Al}/(\text{Al}_3\text{Ti} + \text{Al}_2\text{O}_3)$ composite system increasing the reaction temperature can lead to the formation of large amount of intermetallic compounds as well as porosity during stir casting process. Due to this microstructure homogeneity of the composite is compromised and tensile properties are degraded. Effect of alloying is very crucial in composite system such as Al-Mg/TiO_2 where alloying element Mg react with oxygen to form MgO . Similarly Al_3Ti is also formed due to reaction between Al and TiO_2 particles. Formation of both compounds decrease the work hardening exponent thereby altering the fracture surface from pure ductile in case of Al-Mg alloy to mixed ductile-brittle surface for in-situ composite (Azamiya *et al.*, 2019). Overall one needs to optimize the processing parameters as well as composition of precursors to obtain a good in-situ composite.

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Accumulative Roll Bonding Route for Composite Materials Production

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Introduction

Metal matrix composites (MMCs) are an important engineering material required in this current scenario for many industrial applications such as structural, marine, aerospace, and automobile. The consideration and preference given to MMCs are becoming increased owing to their higher mechanical properties, namely strength-to-weight ratio at both room temperature and high temperature, fatigue resistance and tribological properties (Rosso, 2006; Miracle, 2005; Kaczmar *et al.*, 2000). Particulates, whiskers, and fibers are the various categories of reinforcements used to improve the properties of MMCs. Among these reinforcements, particulates are highly emphasized because the combination of metallic properties (high strength and ductility) and rigid ceramic properties (high thermal stability, isotropic properties, and modulus) suits for higher load carrying applications (Taha, 2007). Among the spectrum of existing methods for producing MMCs, casting (classification: stir/in-situ/compo/squeeze/centrifugal) is the predominant one due to the following reasons: (1) Produce desired shape of components, (2) easy of fabrication, (3) bulk manufacturing, and (4) affordable production cost (Muralidharan *et al.*, 2018; Ramkumar *et al.*, 2015; David Raja Selvam *et al.*, 2018). However, the wettability of reinforcement in the matrix, proper distribution of ceramic particles, non-porous and interfacial reaction between matrix, and reinforcements are the challenges to be achieved by the casting technique (Rajan *et al.*, 2016). The aforementioned challenges are arising due to mismatch between coefficients of thermal expansion and densities between the matrix and the ceramic particles which lead to less ductile and poor toughness. Hence, solid state processing (SSP) is the only technique to overcome the issues because the work piece does not melt during processing (Harris, 1999; Clyne, 2001).

There are two solid state methods coming under the category of SSP which are powder metallurgy (P/M) (Angelo and Subramanian, 2008) and friction stir processing (FSP) (Mishra and Mahoney, 2007). In P/M technique, the composite powder particles are synthesized using mechanical alloying (MA) process to get homogeneous mixture followed by compaction (classification: cold or hot compaction, Sivasankaran and Alaboodi, 2016; vacuum hot pressing, Ramkumar *et al.*, 2017; spark plasma sintering (SPS), and reactive SPS, Kieback, 2011; Dudina and Mukherjee, 2013). Though P/M is an efficient technique, it is not an economical one, i.e., it requires higher production cost and time and consumes more energy to manufacture the composites (Suryanarayana and Al-Aqeeli, 2013). The next one is FSP, it has an ability to produce three-dimensional material flow to change the initial microstructure by dispersing the ceramic reinforcement particles homogeneously (Rathee *et al.*, 2018; Zhang *et al.*, 2012). The severe deformation takes place by the combined action of frictional heat and mechanical action of the revolving tool. However, deterioration of tool, numerous trials required to optimize the process parameters, multiple passes required for proper dispersion and defect free joints are the disadvantages in FSP technique (Ma *et al.*, 2008).

Accumulative Roll Bonding

Conventional fabrication technique such as stir casting, powder metallurgy, friction stir processing are capable of producing composites. However, the homogeneous distribution of reinforcement particles and cluster-free particles in the composite are hard to obtain (Fattahi *et al.*, 2013, 2015). Hence, a novel and recent technique, accumulative roll-bonding (ARB), one of the SPD technique, evolved by imposing higher plastic strain on metals sheets by rolling process. This technique is evolved to produce MMCs which not only reduce the clustering of reinforcement particles and improve the uniform dispersion but also leads to generation of ultrafine or nano-sized grain materials, laminated composites, and strengthening of materials as well (Tsuji *et al.*, 2013; Saito *et al.*, 1999). The basic principle of operation of ARB are as follows: (1) Dimensioning, (2) surface preparation, (3) dispersing the reinforcement particles, (4) stalking and preheating the sheets, and (5) roll bonding (Ramkumar and Natarajan, 2018). Fig. 1 shows the production process of MMCs through ARB technique. Initially, the sheets for required size, i.e., length $\times$ breadth $\times$ width are cut according to the desirable dimensions. Next, surface preparation, i.e., in common practices such as wire brushing, scratching, filing, or knurling are performed over the sheets, which increases the surface roughness and removes the contaminant layer (i.e., oxide and age hardened layer) over the surface. Simultaneously, alkaline cleaning has to be done either using ethanol or acetone which helps to remove weak hydrocarbon layer (i.e., grease, wax, and other dirt over the surface). Then, the hard-ceramic particles are dispersed over the scratched sheets using gas atomizer. The sprayed reinforcement particles are mechanically interlocked within the scratched surface. Then fourth step, stalking the sheets one over another like sand-witch form. At last, roll bonding takes place. After adjusting/fixing the roll gap, roller speed and pressure, the prepared sheets are passed into the rollers. This process is repeated limitlessly till achieving the expected properties. The induced plastic strain in that material initially makes the grains elongated heavily and breaks the grain into ultrafine or nano-level, in parallel the dispersed reinforcement particles gets settled down within the asperity zone uniformly (Jamaati *et al.*, 2014a; Kazemi Talachi *et al.*, 2011; Darmiani *et al.*, 2013).

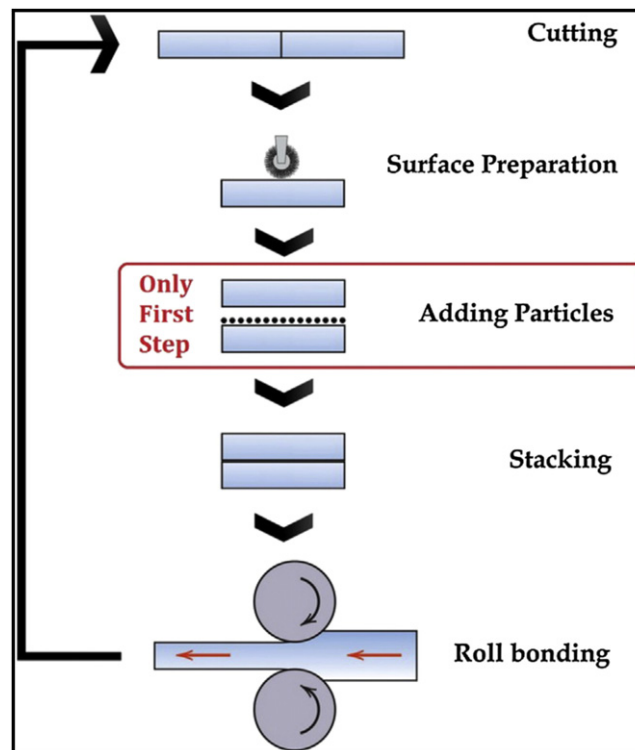


Fig. 1 Schematic illustration showing the principles of the ARB process. Reproduced from Jamaati, R., Naseri, M., Toroghinejad, M.R., 2014a. Wear behavior of nanostructured Al/Al₂O₃ composite fabricated via accumulative roll bonding (ARB) process. *Materials and Design* 59, 540–549.

The mechanisms acting behind the ARB process are: (1) Atom to atom bonding between the sheets, (2) film theory, i.e., breaking up of oxide layers over the surface during rolling, where formed oxide layer gets cracked and widen due to further rolling. In general, metal plastically deforms and elongates during rolling. In the widen zone, metal to metal contact takes between the overlapped sheets by elongation of grains and reinforcement particles get bonded with the sheets. Then the relationship between: (3) Bond strength with deformation induced localized heating, and (4) bond toughness and shear band is established (Ahmadi *et al.*, 2014).

On other hand, another process used to produce composite sheets is continuous annealing and roll bonding (CAR). The fabrication procedure of CAR and ARB are similar to each other. However, in CAR process, the stalked/roll bonded sheets are annealed to the recrystallization temperature before each pass of rolling whereas the annealing is not done in ARB process. CAR process helps to increase the formability and ductility of the composite strips and ARB is to achieve higher mechanical strength such as ultimate tensile strength (UTS) of the composite strips than CAR process (Dehsorkhi *et al.*, 2012).

Matrix and Reinforcement Used

Table 1 indicatively summarizes the matrix sheet (base metal) with its dimension, reinforcement particle chosen with its size and wt% taken, and the process parameters such as rolling speed, temperature, load, and number of passes. Numerous investigations have been carried out on the fabrication of Al, Mg, Cu, Fe, and Ti MMCs fabricated using ARB technique by reinforcing with aluminum oxide (Al₂O₃), multi-walled carbon nanotubes (MWCNT), boron carbide (B₄C), silicon carbide (SiC), and graphene nanosheets (GNS) (Nasresfahani and Shamanian, 2018; Fattah alhosseini *et al.*, 2016; Jamaati and Toroghinejad, 2014; Liu *et al.*, 2015; Yoo *et al.*, 2012; Isfahani *et al.*, 2016; Jamaati *et al.*, 2014b; Karimi and Toroghinejad, 2014).

Optical microscopic images of Cu–SiC_p composite fabricated using CAR process in a particular study (Ghaderi *et al.*, 2013) shown in **Fig. 2**. **Fig. 2(a)** depicts the non-homogeneous dispersion of SiC_p in the Cu after third cycle. This specimen comprises large SiC_p reinforcement, particle-less zones, and more clustered particles. Hence the distribution of second phase particles is increased by increasing the number of passes, which is shown in **Fig. 2(b–c)**. After nine passes, uniform dispersion of SiC_p was obtained due to annealing between each pass. Annealing treatment makes the strips more formable and ductile, which helps the particle to move freely in the matrix and fragments the clustering nature among the particles.

Fig. 3 (SEM image) depicts the particular study of 5 wt% SiC distribution in the Ti matrix in RD–TD plane for the first bonded layer manufactured by ARB process (Karimi and Toroghinejad, 2014). Right side images represent the rectangular regions of the left side images in higher magnification. The variation in SiC distribution with ARB cycles was nearly similar for all three powder contents. After second pass, improper dispersion of particulates with clustered nature, particle-free zones, porosities in the Ti/SiC

Table 1 Salient works conducted by various researchers

Ref.	Year	Base metal	Reinforcement			Sheet dimension (mm ³)	Rolling speed	No. of passes	Temperature	Load (tons)	% reduction
			Chosen particles	Particle size	Vol. fraction						
(Nasresfahani and Shamanian, 2018)	2018	Al	Al ₂ O ₃	20 μm	4.4 wt%	500 × 100 × 2	–	10	Room temperature	40	60% then 30%
			MWCNT	10 μm	0.3 wt%						
(Fattah alhosseini <i>et al.</i> , 2016)	2016	Al 1050	B ₄ C	50 μm	1.0 wt%	150 × 50 × 1	35 rpm	12	Room temperature	20	50%
			SiC	50 μm	2.5 wt%						
(Jamaati and Toroghinejad, 2014)	2010	Cu	Al ₂ O ₃	<2 μm	15 wt%	200 × 50 × 1.5	–	9	Room temperature	20	50%
(Liu <i>et al.</i> , 2015)	2015	Cu	GNS	10 nm x 50 μm	0.05 mg m ⁻²	150 × 25 × 1	0.34 m s ⁻¹	8	Room temperature	20	50%
(Yoo <i>et al.</i> , 2012)	2012	Mg	SiC	50 nm	2 wt%	125 × 55 × 1	1 m min ⁻¹	14	Room temperature	–	50%
(Isfahani <i>et al.</i> , 2016)	2016	Mg (AZ31)	ZrO ₂	50 nm	1 wt%	300 × 200 × 2	3 m min ⁻¹	8	Room temperature	20	50%
(Jamaati <i>et al.</i> , 2014b)	2014	Fe	SiC	50 nm	2 wt%	150 × 50 × 0.7	–	4	Room temperature	–	75%
(Karimi and Toroghinejad, 2014)	2014	Ti	SiC	–	1.5 wt%	200 × 50 × 1	4.5 m min ⁻¹	7	Room temperature	–	50%
					3 wt%						
					5 wt%						

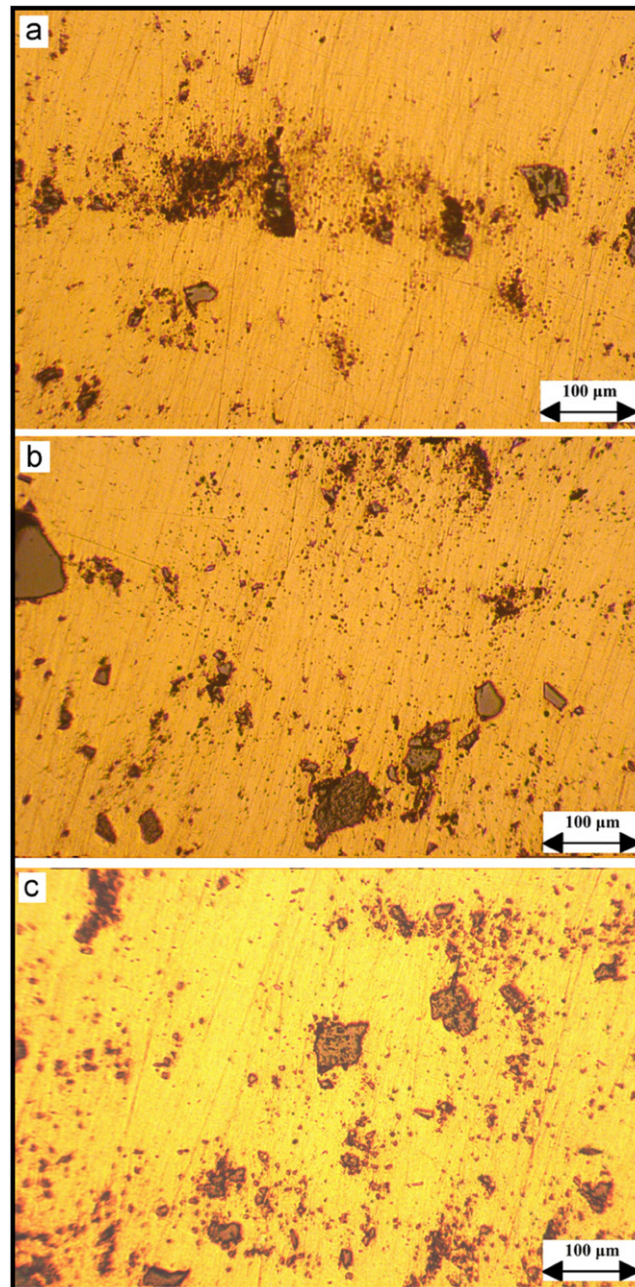


Fig. 2 Optical micrographs of RD–TD plane of copper/2 vol% silicon carbide MMC produced by the (a) third, (b) fifth and (c) ninth cycles. Reproduced from Ghaderi, O., Toroghinejad, M.R., Najafizadeh, A., 2013. Investigation of microstructure and mechanical properties of Cu–SiCP composite produced by continual annealing and roll-bonding process. *Materials Science & Engineering A* 565, 243–249.

interface, fracturing, and debonding of particles were observed. SiC dispersion after fourth cycle was somewhat improved and dispersed comparatively well. Nevertheless, agglomeration could be seen in many areas at this stage of the process as well. Furthermore, broken particles were observed in clustered areas after second and fourth cycles. Cracked particles cannot effectively tolerate any load and act as voids (Chawla *et al.*, 1998), which leads to cracking and breakage in the composite compared with conventional materials. After sixth and eighth cycles, uniform distribution of particles was improved. Especially, after eighth pass, particles distribution was significantly improved without any noticeable fracturing, deboning of particles and porosities. Additionally, clustered particles and particle-free regions were reduced (Alizadeh *et al.*, 2012).

SEM micrographs (Isfahani *et al.*, 2016) of 1 vol% ZrO₂/AZ31 composite produced by ARB at the first and eighth cycles in Fig. 4. After first cycle, it is clearly observed that non-uniform distribution and clustering of ZrO₂ nanoparticles in the matrix. After eight cycles, all the clusters were disappeared and a uniform dispersion of reinforcement into the matrix was obtained (Fattahi *et al.*, 2015).

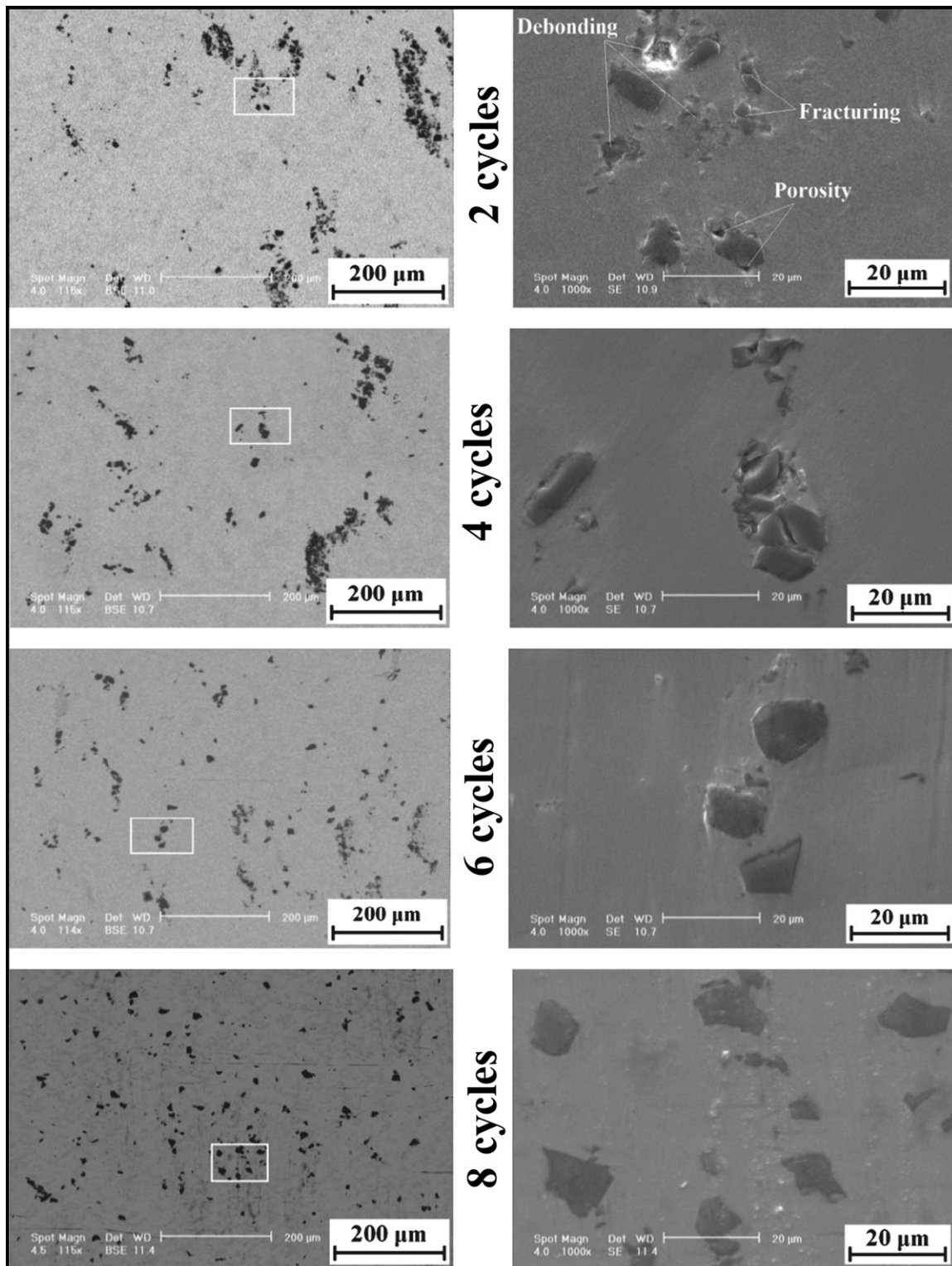


Fig. 3 Particles distribution for composite produced by ARB process with the final composition of Ti-5 vol% SiC in RD-TD plane. Right side images represent the rectangular regions of the left side images in the higher magnification. Reproduced from Karimi, M., Toroghinejad, M.R., 2014. An alternative method for manufacturing high-strength CP Ti-SiC composites by accumulative roll bonding process. *Materials and Design* 59, 494–501.

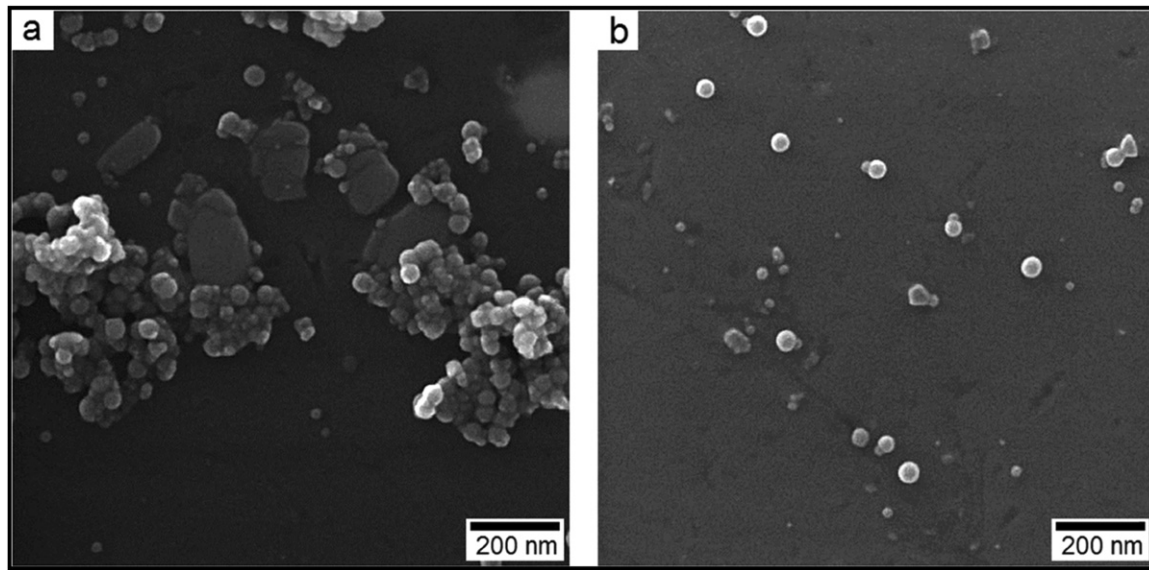


Fig. 4 SEM micrographs of the 1 vol% ZrO_2 /AZ31 composite produced by ARB at the: (a) First and (b) eighth cycles. Reproduced from Isfahani, Z., Hashempour, F., Amirkhanlou, F., 2016. Fabrication and properties of ZrO_2 /AZ31 nanocomposite fillers of gas tungsten arc welding by accumulative roll bonding. *Achieves of Civil and Mechanical Engineering* 16, 397–402.

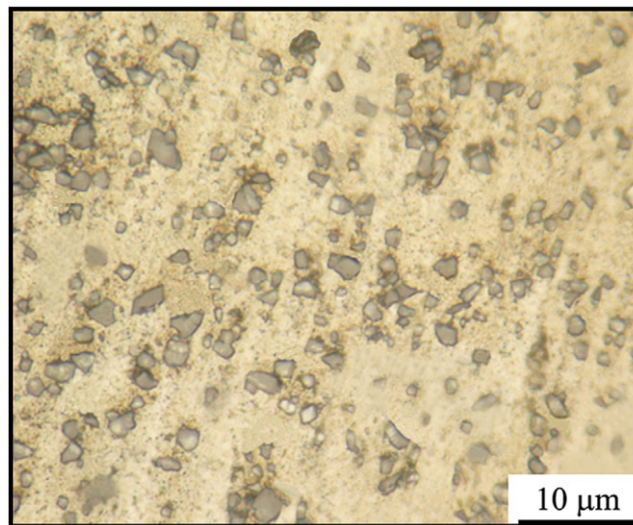


Fig. 5 OM micrographs of the Al/10 vol% B_4C composite after 8 cycles. Reproduced from Alizadeh, M., 2011. Strengthening mechanisms in particulate Al/ B_4C composites produced by repeated roll bonding process. *Journal of Alloys and Compounds* 509, 2243–2247.

In general, following are the difficulties occur during ARB process, when: (1) Matrix is moved to elevated temperature, (2) increase in volume fraction and (3) reinforcement size to nano-level (Yoo *et al.*, 2012). In CAR process, when the rolled bonded sheets attain high temperature, strain hardening takes place during rolling process gets nullified. This technique helps to increase the formability and ductility of the specimen but decreases the mechanical property such as UTS of the specimen. Increase in volume fraction of micron-sized particles leads to decrease in % elongation (i.e., ductility of the composite), micron-sized particles pave the way to propagation of crack at the matrix and reinforcement interfaces. Ultrafine or nanoparticles reduce the particle-free zone between the sheets which results in reduction in bonding area between the sheets (Jamaati *et al.*, 2010; Amirkhanlou *et al.*, 2014).

Microstructural Evolution

Fig. 5 shows the optical microscopic image of Al/10 vol% B_4C particulates composites produced by the RRB process (Alizadeh, 2011). This image was captured in RD–ND direction of the composite. After sixth cycle, the absence of porosities and cracks in the

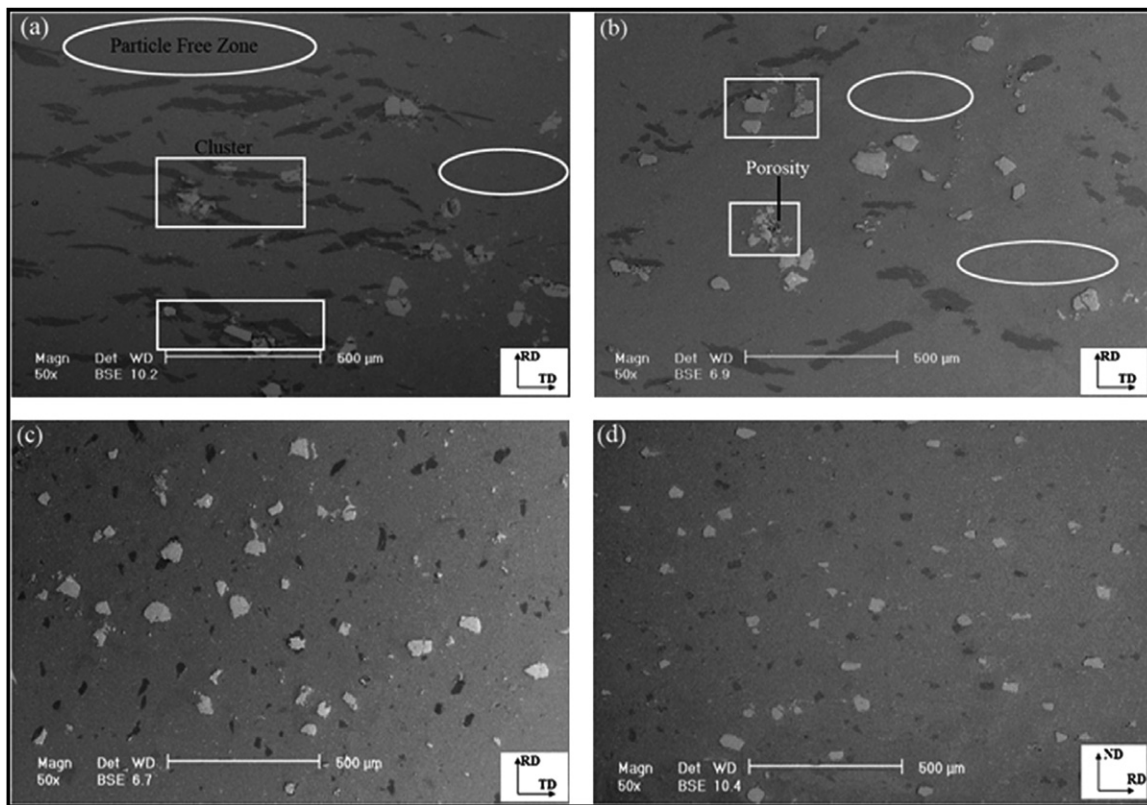


Fig. 6 SEM micrographs of Al_2O_3 and TiC particles distribution for RD–TD plane of (a) 1st cycle, (b) 4th cycle, (c) 8th cycle and (d) RD–ND plane of 8th cycle. Reproduced from Dehkordi, H.F., Toroghinejad, M.R., Raeissi, K., 2013. Fabrication of $\text{Al}/\text{Al}_2\text{O}_3/\text{TiC}$ hybrid composite by an oxidizing and accumulative roll bonding processes and investigation of its microstructure and mechanical properties. *Materials Science & Engineering A* 585, 460–467.

composite is observed. Still, agglomerations and clustering of B_4C were observed and which comprises porosities and cracks within the composite which are deleterious to the mechanical properties.

Fig. 6(a–d) demonstrate the particle scattering of $\text{Al}/1.6 \text{ vol}\% \text{ Al}_2\text{O}_3/1 \text{ vol}\% \text{ TiC}$ hybrid composite in RD–TD planes in various cycles of ARB process (Dehkordi *et al.*, 2013). **Fig. 6(a)** shows the occurrence of departing and fracturing phenomenon in the brittle alumina layer after first cycle. It is clearly observed that the coarse Al_2O_3 fragments with small amount of TiC in Al matrix. Besides, large particle-free zones and agglomeration has been identified. Then, the Al_2O_3 layers were broken down into smaller particles. However, the generation of large particle-free zones and clustering of TiC particles with porosity were present due to further TiC addition, after 4th cycle (**Fig. 6(b)**). Increasing the cycle to eighth time results in complete disappearance of particles – Free zones and remarkable improvement in uniformity of particles distribution in Al matrix (**Fig. 6(c)**). **Fig. 6(d)** witnessed relative uniformity in particles distribution in the Al matrix. In accordance with **Fig. 6(c–d)**, absence of porosities, debonding between Al layers and interfaces of Al and reinforcements after the eighth cycle are noticed. Based on the obtained micrographs, it can be summarized that, by increasing the number of cycles, the uniform dispersion of reinforcement particles in Al matrix can be obtained.

SEM micrographs of Al/SiC composite produced by RRB process in various cycles in a particular study (Alizadeh and Paydar, 2009) are shown in **Fig. 7**. The microstructural changes were observed in the cross-section of the composite parallel to the rolling direction (TD). It can be clearly noticed that the porosities are terminated at the interface by increasing the number of cycle, i.e., deformation due to roll bonding allows the matrix to flow to the matrix reinforcement interfaces and leads to disappearance of discontinuity at the interface regions. Matrix flow also breaks the reinforcement clustering and separates each particle which improves the uniformity of SiC particles distribution in the overall matrix (**Fig. 7**). **Fig. 7(a)** point out that the SiC particles, located in the interface, with increase in the number of cycles, their position at the interface is gradually moved to the bulk matrix (**Fig. 7(c)**). Hence from **Fig. 7**, it can be summarized that, increasing the passes results in nullification of porosities at the interface nearly zero percent, uniform distribution of SiC particles in the bulk sheets and the layered structure at interface is modified and changed to be a regular Al/SiC composite completely.

In general, graphite (Gr) is a solid lubricant and increases the wettability between the matrix and reinforcement which leads to improvement in wear resistance by working as a solid lubricant but hinders the bonding quality. Hence, it is well known that debonding at interface increases with the addition of Gr content which can be overcome by increasing the number of passes. In particular (Reihanian *et al.*, 2017), SEM micrographs in **Fig. 8(a–d)** depicts the evolution and improvement of the bonding of

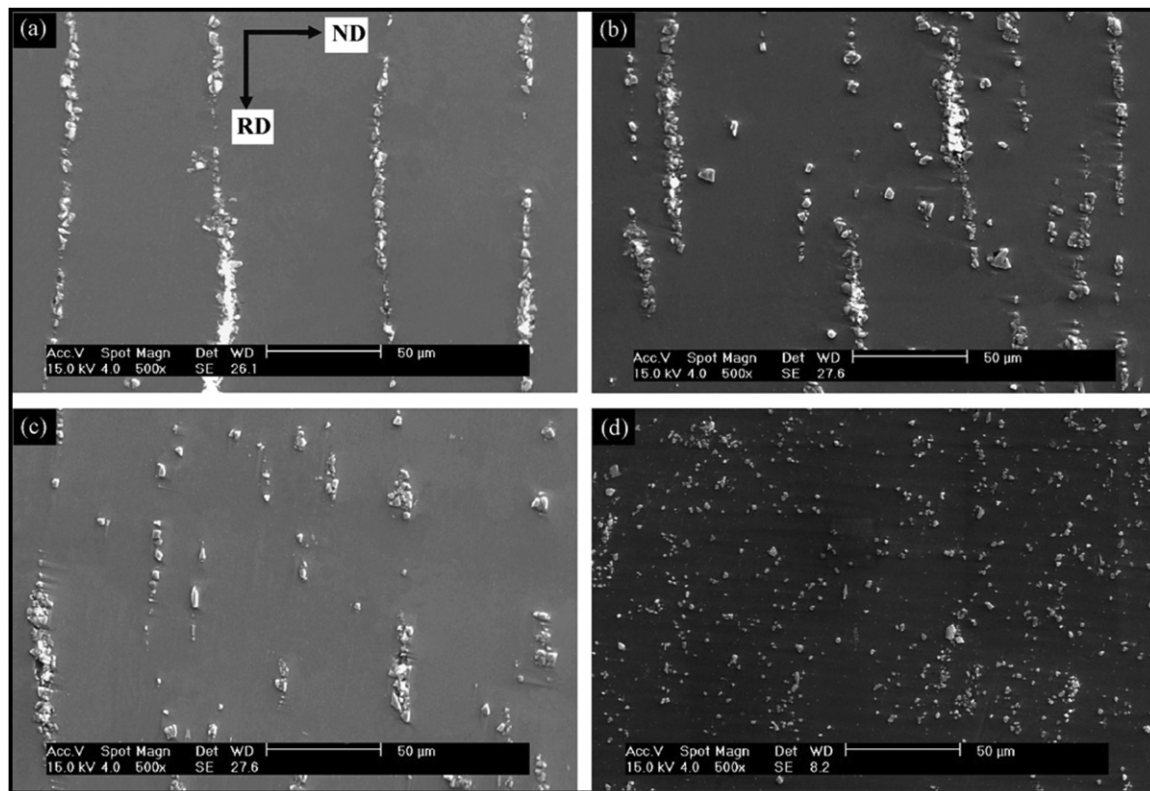


Fig. 7 SEM micrographs of Al/SiC composites microstructures after (a) first cycle, (b) third cycle, (c) fourth cycle and (d) Seventh cycle. Reproduced from Alizadeh, M., Paydar, M.H., 2009. Fabrication of Al/SiCP composite strips by repeated roll bonding (RRB) process. *Journal of Alloys and Compounds* 477,811–816.

nanostructured Al–95 SiC–5Gr (95:5) composite after two, four, six, and eight cycles of ARB, respectively. **Fig. 8(a–b)** shows the improved bonding quality but there is still considerable debonding at layer interfaces. After the eighth cycle, the bonding quality is better in all composites which is witnessed from **Fig. 8(c–d)**. In accordance with film theory, during surface preparation, the surface layer gets work hardened and broken due to the pressure applied during ARB process, leads to several surface cracks. When the as received metals are passed between the rollers, bonding is obtained when the metal surfaces touch each other. In general, incorporated reinforcement particles prevent the bonding process. Nevertheless, flow of matrix over the particles with the force can generate good bonding between the layers and also the metal flow nullifies the cracks and porosities at the interface.

Fig. 9 shows the SEM micrograph and EDS distribution map of O and Al produced after eight cycles of ARB in Al–Al₂O₃ composite. Mechanical properties of MMCs rely on proper distribution of the reinforcement particles (Topic *et al.*, 2009; Sun *et al.*, 2009). It is clearly observed from the images that the reinforcement particles are distributed uniformly in the fabricated composite sheets.

The X-ray 3D image (Zheng *et al.*, 2017), of Li_{6.75}La₃Zr_{1.75}Nb_{0.25}O₁₂ (LLZNO)/Al composites after 10 ARB cycle (**Fig. 10**), specifies that the dispersion of Li, La, Zr, Ni, and O appear to be homogeneous (designated by yellow dots), which provides further evidence that a uniform distribution of LLZNO particles in AMCs is formed successfully after 10 ARB cycles. The measured volume ratio is highly correlating with the original ratio of introduced reinforcement phases. This can be attributed to the high deformability of Al matrix and the multi-step rolling, cutting, stacking, and recycling of the ARB process.

Fig. 11 shows the EBSD maps of the Al/Al₂O₃/WC composite after eight cycles of ARB (Shamanian *et al.*, 2013). The image was captured in RD–TD plane of the specimen. In the grain boundary maps, red and green lines indicate the misorientation angle of HABs more than 15° and LABs of 2–15°. The ultrafine lamellar structure is illustrated in the obtained microstructure which contains convex grain around the particles and fine grains. The fine grains are around 400 nm where their alignment is parallel to RD. **Fig. 11(a–b)** shows the wide bands filled with many black regions which are the bonded interfaces and the regions including the composite particles. It is obvious from **Fig. 11(d)** that the density of LABs is relatively high near the particles.

TEM images (Beni *et al.*, 2013) of the Al/Al₂O₃/B₄C nanocomposite and monolithic Al after 5 ARB cycles is shown in **Fig. 12(a–b)**. The images reveal the significance of grain refinement in the matrix with the addition of hard ceramic particles during ARB. Nano-level alumina and B₄C particles hinder the refinement of grain when added to the matrix. This results in enhancement of dislocation density whereas they can lead to an increased rate in the generation of HAGB areas with strain. As such, a submicron grain structure can be obtained at a considerably lower strain than that of the single-phase alloy (Saito *et al.*, 1999). The reasons for

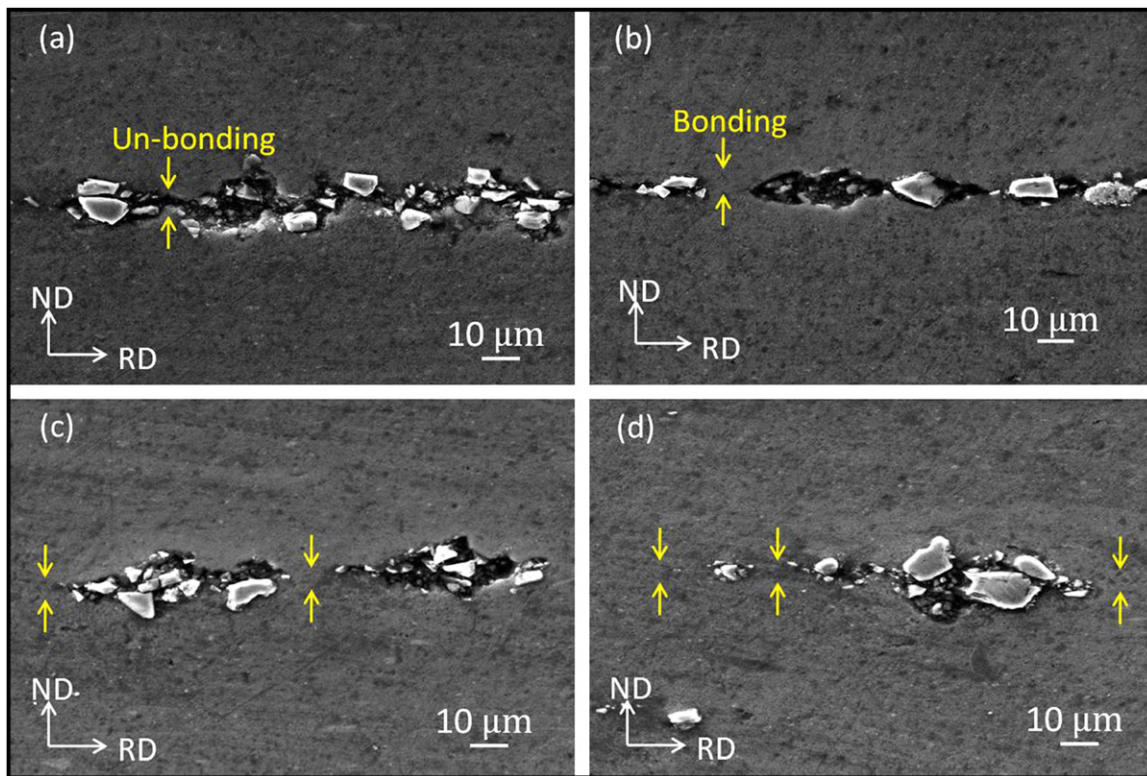


Fig. 8 High-magnification SEM images of the Al/SiC-Gr (95:5) composite after (a) two, (b) four, (c) six and (d) eight cycles. Reproduced from Reihanian, M., Fayezipour, S., Lari Baghal, S.M., 2017. Nanostructured Al/SiC-graphite composites produced by accumulative roll bonding: Role of graphite on microstructure, wear and tensile behavior. *Journal of Materials Engineering and Performance* 26, 1908–1919.

the increase of dislocation density are: (1) Due to presence of ceramic particle in MMCs paves the way for strain incompatibility accommodated at the interface and also increases the local strain of the matrix in the proximity of the particles which enhances the work hardening of the matrix, (2) difference between the thermal mismatch between matrix and reinforcements (Zhang and Chen, 2006), and (3) during deformation, fine reinforcement particles are known to increase the rate of dislocation generation by encouraging the formation of Orowan loops. This will increase the work hardening rate and dislocation density (Apps *et al.*, 2005).

TEM microstructure (Liu *et al.*, 2013) of the annealed Al, Al after ARB and Al/3 vol% WC composite after ARB are shown in Fig. 13(a–c). Fig. 13(a) shows that the grain size in annealed Al 1060 is significantly large that a whole grain could not be observed. Al 1060 grains became finer (0.7 nm) after 13 cycles of ARB as inferred from Fig. 13(b). The deformed structure comprises substantial amount of dislocations (Hansen, 2004). Accordingly, grain refinement and strain hardening by dislocations are the two key strengthening mechanisms of the Al sheets after 13 cycles. Adding 3 vol% WC particles to Al matrices, geometry necessary dislocations were introduced. More dislocations are generated at the WC–Al interface (Fig. 13(c)). Besides grain refinement and strain hardening, dispersion strengthening promotes the strengthening of the matrices. Because the hard particles hinder the dislocation motion of the matrix grains which results in an increase in dislocation density near the interfaces (Fig. 13(c)).

Effect of Process Parameters

Effect of Passes

Generally, high cohesive energy leads to increase in the occupancy of surface area and tendency of clumping together which forms larger cluster and agglomerated particles. The presence of large clustered particles in the fabricated composite leads to decrease in bonding between matrix and reinforcement, which makes the bonding weak in the composite and porous. Hence, it is essential to perform the subsequent ARB process to separate the clustered particles. During roll bonding, matrix deforms plastically, extends towards the rolling direction by flowing through cluster of particles, at the same time, the dense reinforcement clusters were diffused into fine particles and result in the formation of uniformly distributed MMCs. This phenomenon shows that increase in number of ARB cycles, the large clusters were separated and dispersed homogeneously in the composite (Chandrasekar *et al.*, 2009).

Fig. 14(a–f) demonstrate the SEM micrograph of the Al hybrid composite reinforced with 1.5 and 1.6 vol% of B_4C and Al_2O_3 , respectively, produced by ARB technique (Toroghinejada *et al.*, 2014). After first cycle of ARB, highly clustered, large agglomerated particles with some porosity were identified. The dispersion of B_4C and Al_2O_3 particles in Al matrix was completely non-uniform

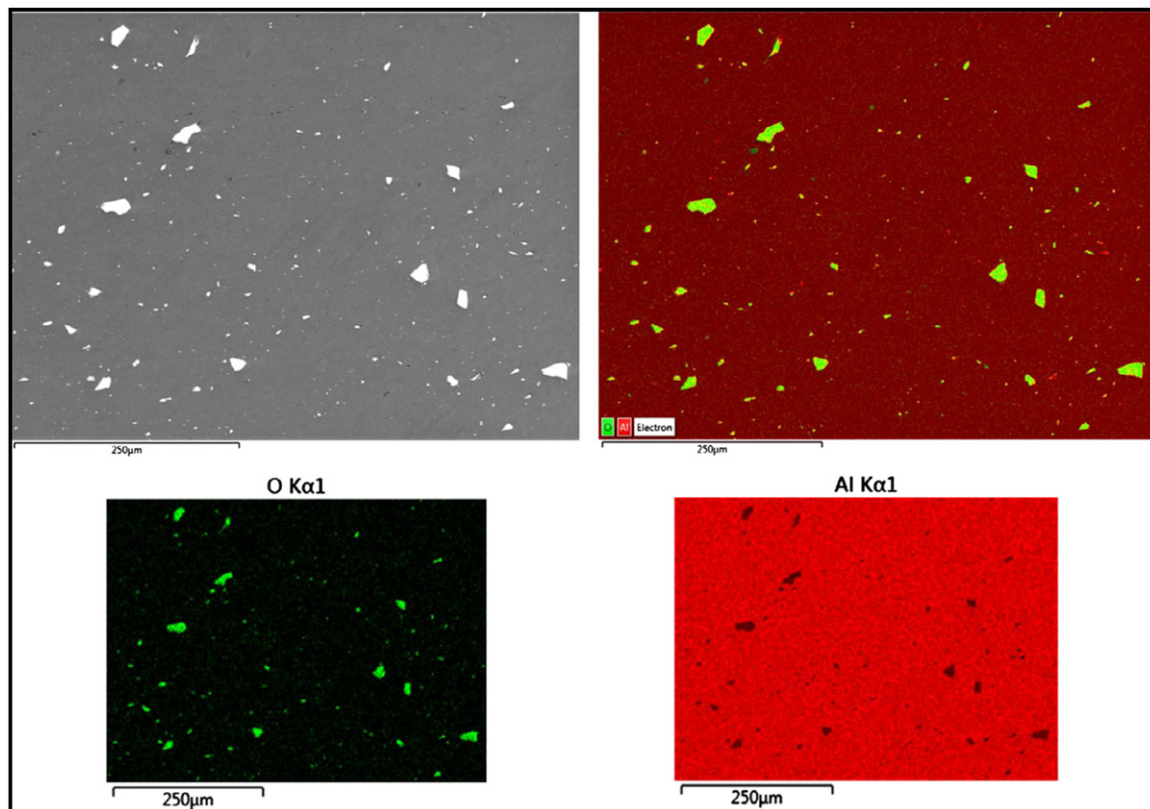


Fig. 9 EDS analysis showing distribution map of O and Al in the representative SEM image of Al-Al₂O₃ composite produced by the accumulative roll bonding process after eight cycles Reproduced from Shamanian, M., Mohammadnezhad, M., Szpunar, J., 2014. Texture analysis of a friction stir welded ultrafine grained Al-Al₂O₃ composite produced by accumulative roll-bonding. *Journal of Alloys and Compounds* 615, 651–656.

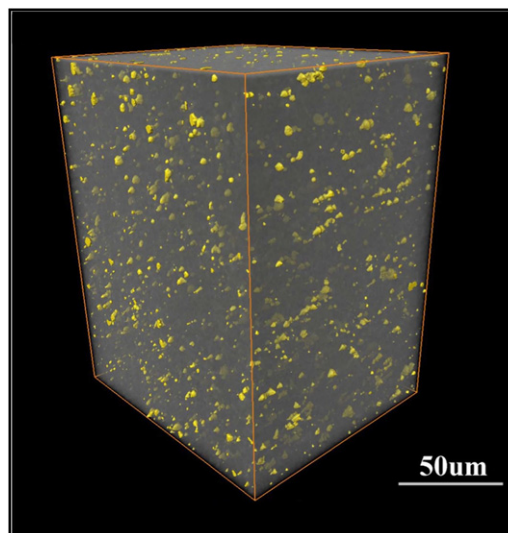


Fig. 10 X-ray 3D image of LLZNO/Al composites. Reproduced from Zheng, W., Gao, Y.X., Wang, X.P., *et al.*, 2017. High strength and damping capacity of LLZNO/Al composites fabricated by accumulative roll bonding. *Materials Science & Engineering A* 689, 306–312.

(Fig. 14(a–b)). Likewise, the SEM morphologies (Shamanian *et al.*, 2013) of Al/Al₂O₃/WC composite are depicted in Fig. 15. Large particle free zones, agglomeration and clustering were present due to the agglomerative nature of particles. Besides, existence of big clusters causes the debonding at the interface and makes the composite weak and pore (Fig. 15(a–b)). In both these cases (Figs. 14 and 15), the reinforcement particles were large and porous at interface. In order to remove that, it is required to increase the number of ARB passes. As Al has fewer slip systems, it deforms plastically. Ceramic particles are brittle in nature, gets fractured by

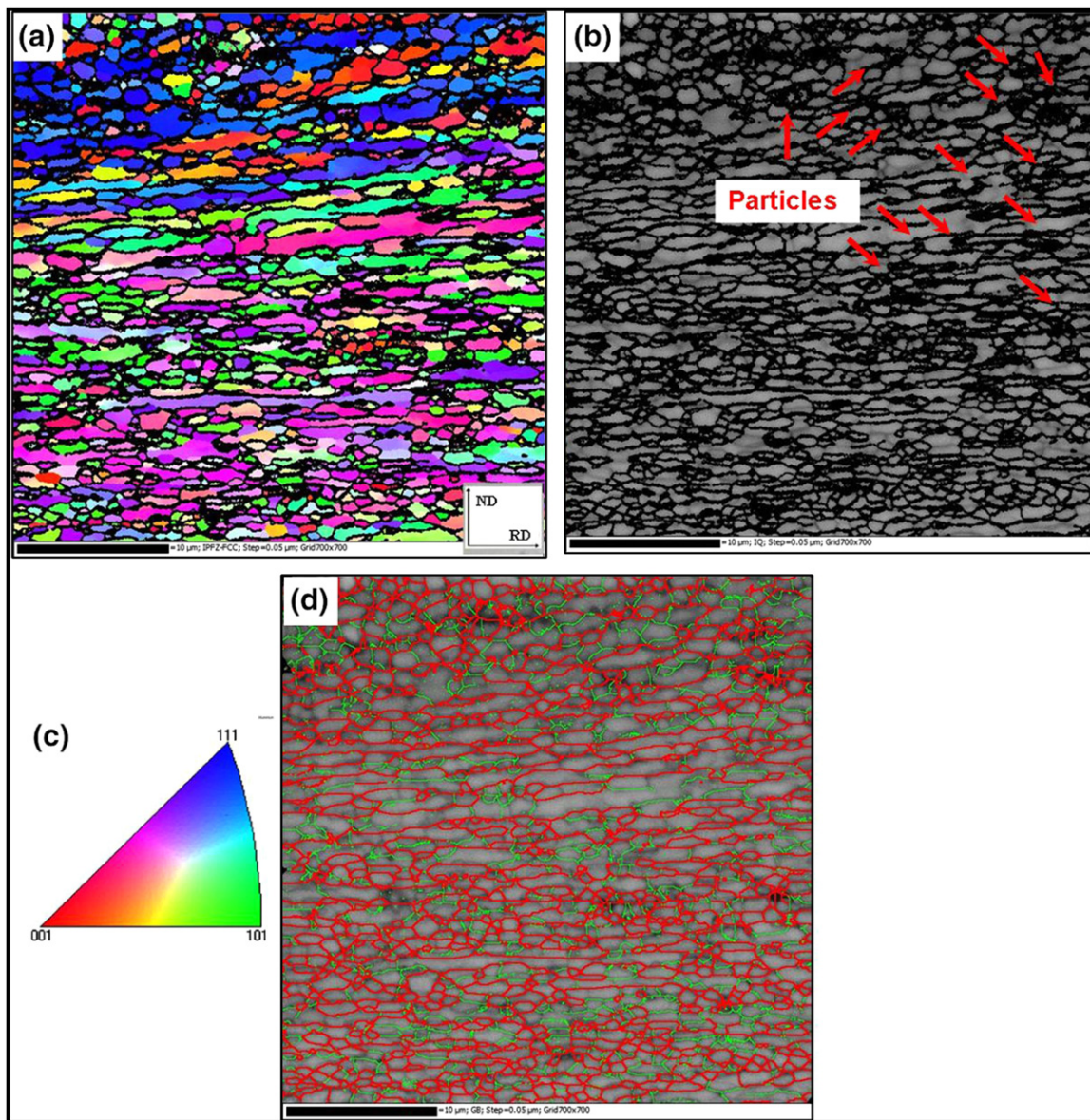


Fig. 11 EBSD maps of the Al/Al₂O₃/WC composite after eight cycles: (a) RD orientation color map (RD map), (b) IQ map, (c) inverse pole figure (IPF) map, (d) boundary misorientation map (GB) Reproduced from Shamanian, M., Mohammadnezhad, M., Szpunar, J., 2013. Production of high-strength Al/Al₂O₃/WC composite by accumulative roll bonding. *Journal of Materials Engineering and Performance* 23, 3152–3158.

applying external stress. After few cycles, large particle free zones and number of agglomerated reinforcements become smaller. As a result, they were homogeneously spread in the entire matrix. In accordance with the aforementioned statement, in **Fig. 14**, porosities and clusters were left and the sheets were modified and changed to a homogeneous hybrid composite. It can be noticed that, both WC and Al₂O₃ layers cluster particles diffused into fine particles and spread uniformly after the eighth pass of ARB (**Fig. 15(g)**).

Effect of Particulate Content

While increasing the particulate content, the following are the difficulties occurring in ARB process. It decreases the net area of the surface which leads to weak bonding between the sheets. Additionally, increase in particle content results in plastic deformation among the accumulated sheets. Hence, it is essential to take some remedy for increasing the particle content. Instead of spraying the reinforcement particles over the sheet, it shall be done over the scratched sheets, i.e., the as received sheets shall be scratched using stainless steel wire brush in order to create pathway for particles to settle down and remove oxide layers over the sheets. This makes the sprayed particles to interlock mechanically inside the scratched pathway in sheets.

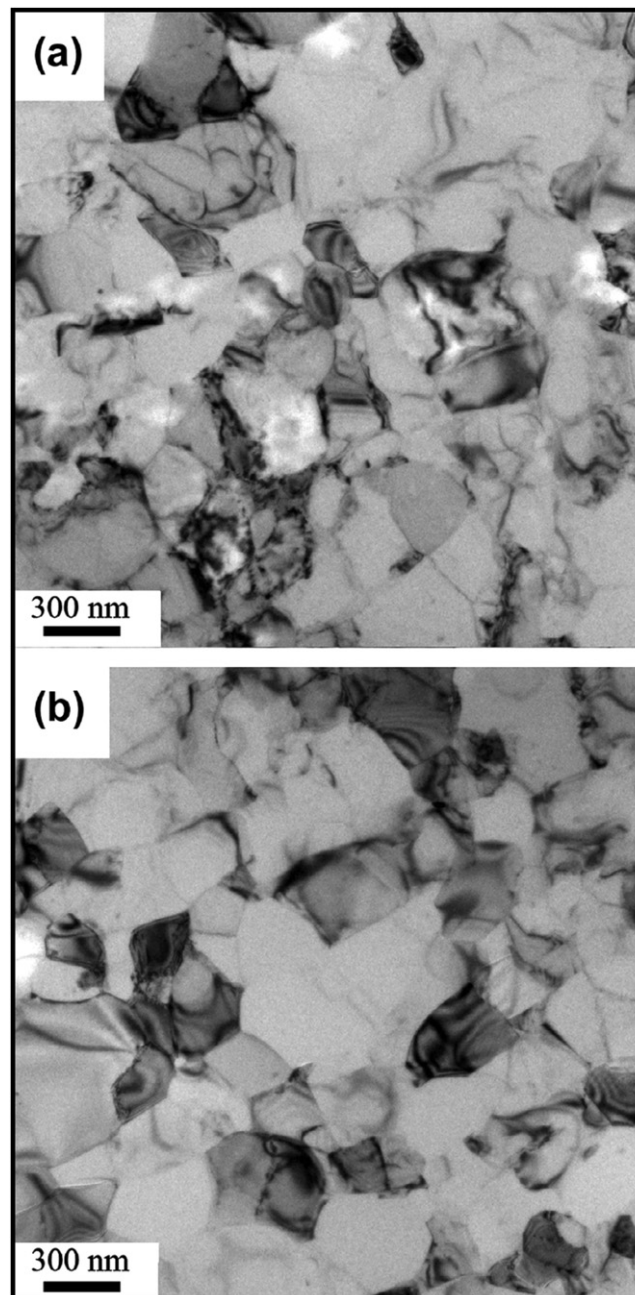


Fig. 12 TEM microstructure of the Al/Al₂O₃-B₄C nano-composite (a) and the monolithic Al (b) after 5 cycles Reproduced from Beni, H.A., Alizadeh, M., Ghaffari, M., Amini, R., 2013. Investigation of grain refinement in Al/Al₂O₃/B₄C nanocomposite produced by ARB. Composites: Part B 58, 438–442.

In between scratching and spraying, the scratched sheets have to be cleaned using acetone to remove the dust particles (Liu *et al.*, 2012).

SEM images (Ramkumar and Natarajan, 2019a) of Al/TiO₂ nanocomposites is illustrated in Fig. 16(a–e). Five layer of Al sheets holds the four layers of TiO₂ nanoparticles. The poor interfacial bonding, clustering and non-uniform distribution of particles in the matrix can be observed after first pass. By increasing the number of passes, detachment of TiO₂ nanoparticles from the matrix interface and locked inside the scratched brushed sheet. Also, annealing between the pass reduces the gap between the Al layer. The transverse section of 3 wt% TiO₂ reinforced Al ARBed sheets are shown in Fig. 16(f). Owing to consequent heating and roll bonding, diffusion among the atoms between the Al sheets takes place. This phenomenon increases the bond strength of the entire ARB strips (Zhang and Chen, 2006). Moreover, it is challenging to see the interface between the Al sheets in higher magnification through SEM analysis.

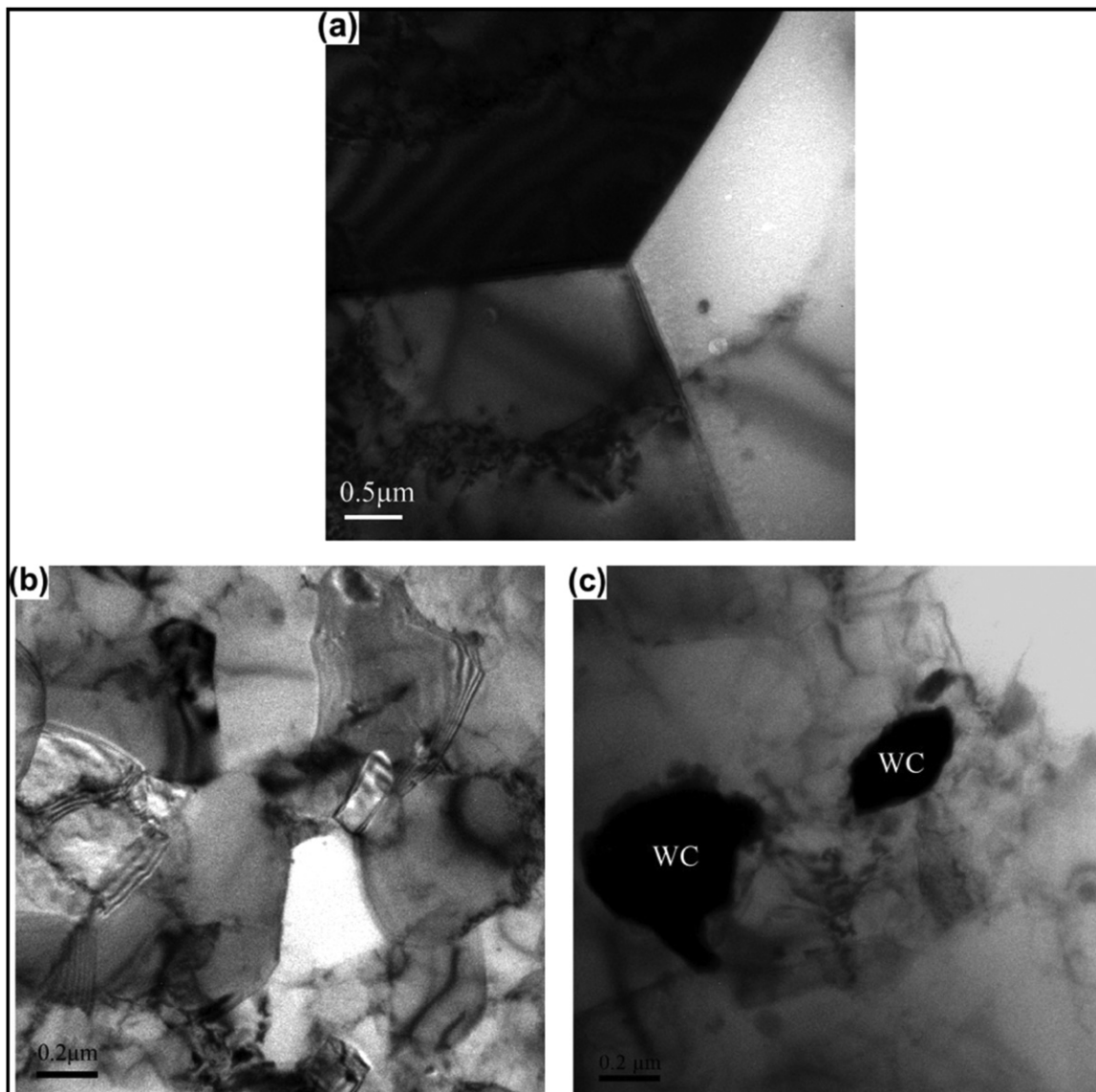


Fig. 13 Transmission electron microscopy (TEM) images of (a) the annealed 1060-Al, (b) ARB of 1060-Al, and (c) Al/3 vol% WC composites. Reproduced from Liu, C.Y., Wang, Q., Jia, Y.Z., *et al.*, 2013. Evaluation of mechanical properties of 1060-Al reinforced with WC particles via warm accumulative roll bonding process. *Materials and Design* 43, 367–372.

Mechanical Behavior

The increase in tensile strength of ARB composites are strengthened by the mechanisms, such as grain refinement and dislocation strengthening/strain hardening. During initial cycles of ARB, increase in tensile strength was achieved by the dislocation strengthening or strain hardening, whereas at final cycles, grain refinement plays a major role for increase in UTS. In fact, during plastic deformation, increase in volume fraction of reinforcement increases more strain hardening, which increases the tensile strength and decreases the ductility. Also, there are three type of strengthening mechanism contributes to the total strength of the matrix, which are grain refinement strengthening, dispersion strengthening, and dislocation strengthening (Ramkumar and Natarajan, 2019b).

Comparison of UTS value using various matrix and reinforcement through ARB technique is given in Table 2. Al 1050 possesses tensile strength of 57 MPa in annealed condition (Fathy *et al.*, 2018). Then same Al strips reached 90 MPa after roll bonded up to 8 cycles. In order to obtain superior mechanical properties, SiC powders were reinforced with the volume pct. of 1, 2 and 4 wt% and their corresponding tensile strength values are 185, 199 and 254 MPa, respectively. The enhancement in tensile strength was due to proper distribution of SiC particles and superior bonding between the matrix layers. In another case (Ahmadi *et al.*, 2014), commercially pure Al holds tensile strength of 91.5 MPa in annealed condition and besides the addition of 0.5, 1 and 2% of SiC as reinforcement, Al_2O_3 is added with a constant wt% of 1.6%. The tensile strength values of 0.5%, 1% and 2% are 259, 272 and

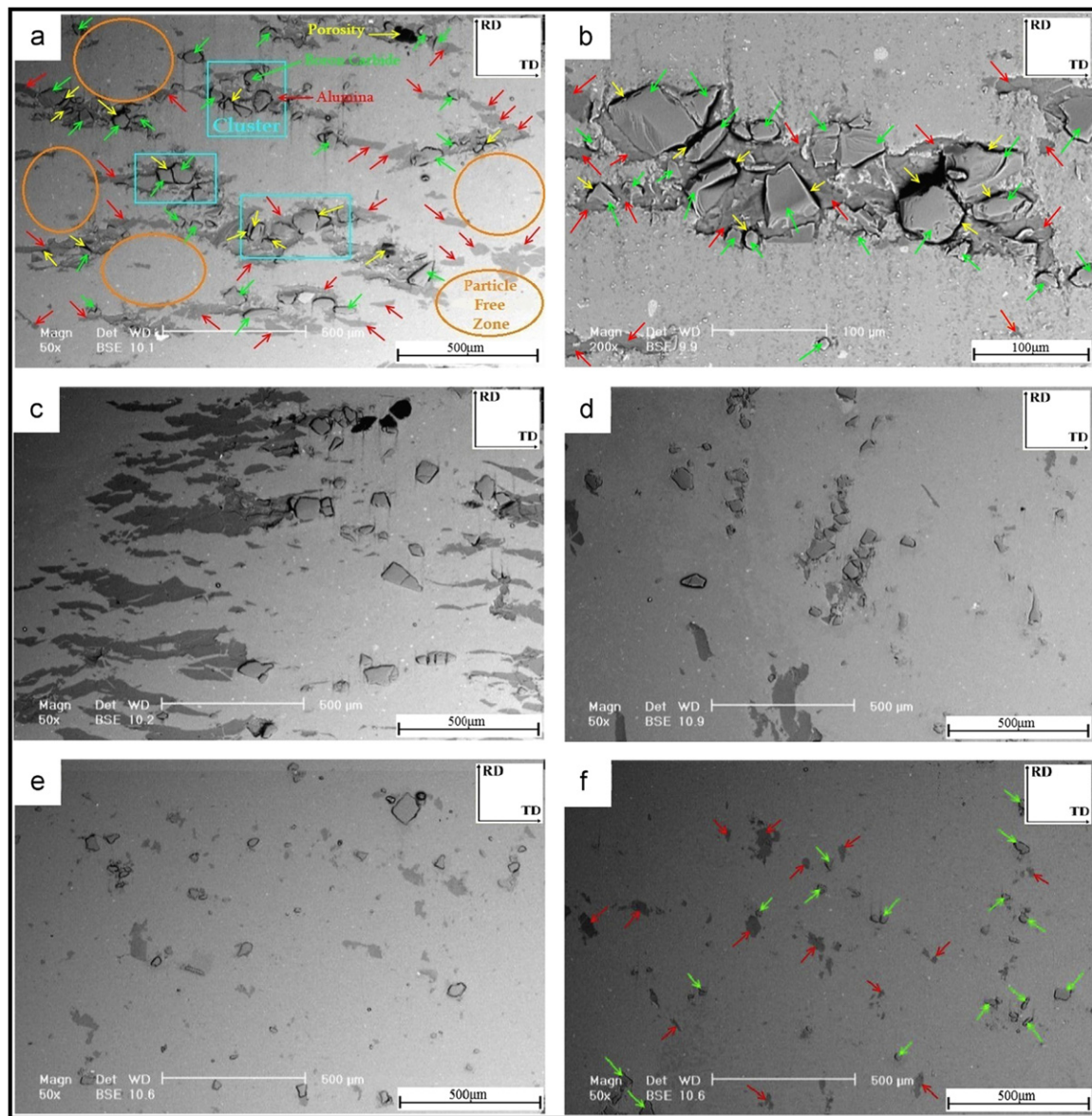


Fig. 14 SEM micrographs of the Al/1.5 vol% B₄C/1.6 vol% Al₂O₃ composites after: (a, b) First, (c) second, (d) fifth, (e) seventh, and (f) tenth ARB cycles Reproduced from Toroghinejada, M.R., Jamaatib, R., Nooryana, A., Edris, H., 2014. The effect of alumina content on the mechanical properties of hybrid composites fabricated by ARB process. *Ceramics International* 40, 10489–10498.

284.4 MPa. Another comparison is made within Al–7% SiC (5 μm) (Alizadeh and Paydar, 2010), Al–3.25% SiC (85 nm) (Rezayat *et al.*, 2012a), Al–0.1% SiC (10 nm) (Schmidt *et al.*, 2011) and Al–4% SiC (5 μm) (Fathy *et al.*, 2018). Among the compared systems, highest tensile strength of 270 MPa has been achieved by Al–3.25% SiC (Rezayat *et al.*, 2012a) owing to the homogeneous dispersion of 85 nm sized SiC particle. Nonetheless, it is most important to consider that 157 MPa was achieved by Al–0.1% SiC by the dispersion of 10 nm SiC particle. Here, just 0.1 wt% could achieve this much. It shows that the nano-sized particles refine the grains than micro-sized particles, which leads to improvement in mechanical property of the materials. The same scenario is occurring in several literature (Ghaderi *et al.*, 2013; Yoo *et al.*, 2012; Jamaati *et al.*, 2018).

The factors influencing the mechanical behavior are elaborated as follows:

- (1) Addition of ceramic particulates: Ceramic particles can improve the maximum stress for dislocation glide and generates further dislocation around the particulates, hence the dislocation mobility decreases during plastic deformation which causes an increase in strength of the ARB MMCs. Matrix reinforcement interfaces are good sites for crack nucleation and propagation. Thus, the ductility of MMCs decreases (Ramkumar and Natarajan, 2019a).
- (2) Homogeneous distribution: Addition of ARB cycles causes the reinforcement distribution in MMCs to be more homogeneous and decreases the gap among the reinforcement particles. This phenomenon leads to improvement in load bearing capacity

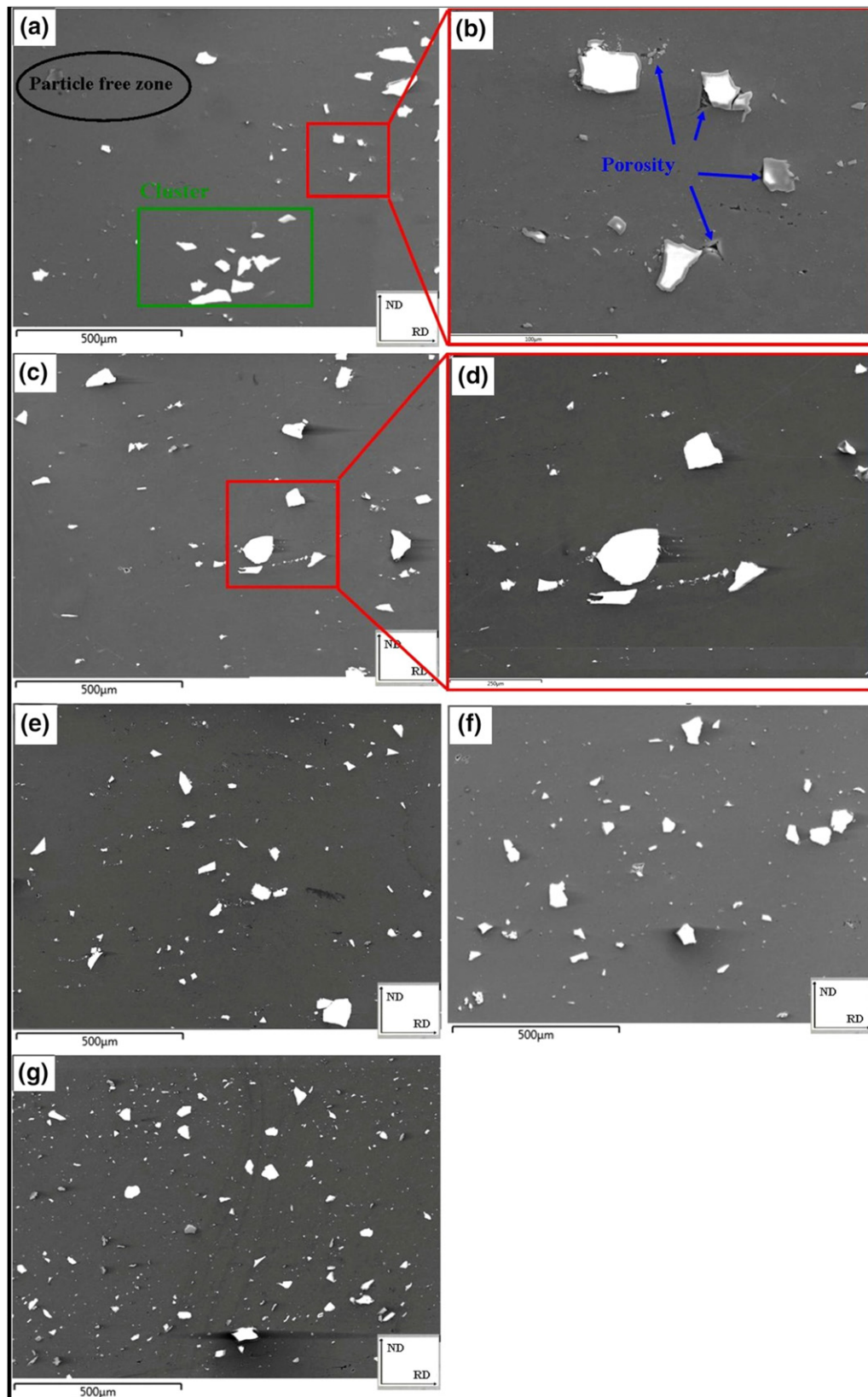


Fig. 15 Typical SEM microstructures of Al/Al₂O₃/WC composite after (a, b) one, (c, d) two, (e) four, (f) six, and (g) eight ARB cycles. Reproduced from Shamanian, M., Mohammadnezhad, M., Szpunar, J., 2013. Production of high-strength Al/Al₂O₃/WC composite by accumulative roll bonding. *Journal of Materials Engineering and Performance* 23, 3152–3158.

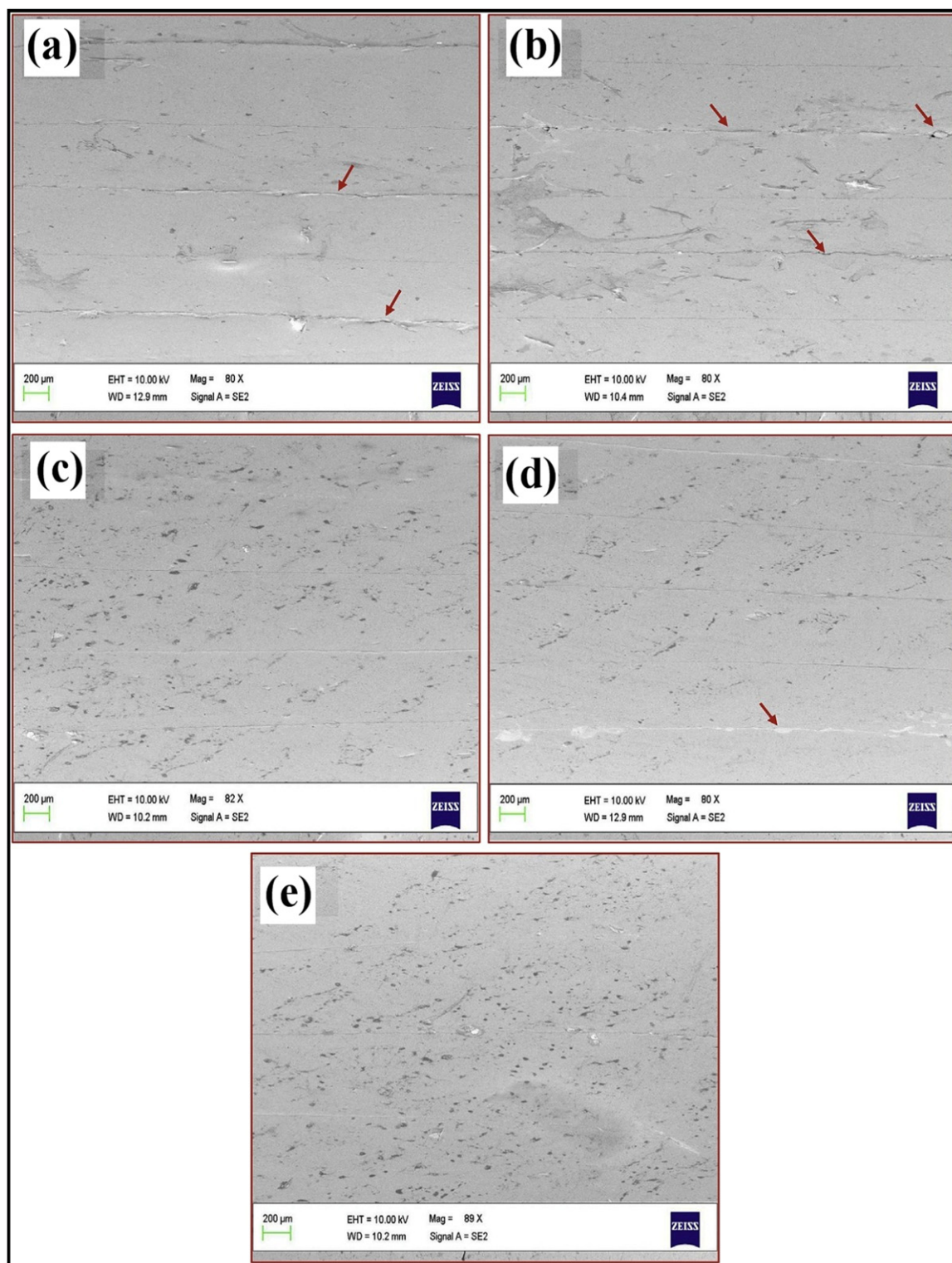


Fig. 16 FESEM micrograph of Al-x wt% TiO₂ nanocomposite sheets after 8 passes of ARB: (a) 0%, (b) 0.75%, (c) 1.5%, (d) 2.25%, (e) 3% (Red arrow indicates debonded region). Reproduced from Ramkumar, K.R., Natarajan, S., 2019a. Effects of TiO₂ nanoparticles on the microstructural evolution and mechanical properties on accumulative roll bonded Al nanocomposites. *Journal of Alloys and Compounds* 793, 526–532.

Table 2 Comparison of ultimate tensile strength using various matrix and reinforcements

Ref.	Year	Base metal	Reinforcement			Yield strength	Ultimate tensile strength	% Elongation
			Chosen particles	Particle size	Vol. fraction			
(Ahmadi <i>et al.</i> , 2014)	2014	Al	SiC	50–75 μm	Annealed Al		91.5	31
			Al_2O_3 (1.6% constant)	24.1 μm	Al–0.5 SiC– Al_2O_3		259	13
					Al–1 SiC– Al_2O_3		272	12
					Al–2 SiC– Al_2O_3		284.4	07
(Fathy <i>et al.</i> , 2018)	2018	Al 1050	SiC	5 μm	Annealed Al		57	38
					Al ARB		90	10
					Al–1% SiC		185	8
					Al–2% SiC		199	7
					Al–4% SiC		254	5
(Alizadeh and Paydar, 2010)	2010	Al 1050	SiC	5 μm	Al–7% SiC		240	16
(Rezayat <i>et al.</i> , 2012a)	2012	Al 1050	SiC	85 nm	Al–3.25% SiC		270	3.5
(Schmidt <i>et al.</i> , 2011)	2011	Al 1050	SiC	10 nm	Al–0.1% SiC		157	–
(Ghaderi <i>et al.</i> , 2013)	2013	Cu	SiC	80 μm	Cu		234	40
					Cu–2 SiC		315	35
(Yoo <i>et al.</i> , 2012)	2012	Mg	CNT	20 nm diameter, 10 – 15 μm length	30 layer composite:			
					ARB 4C (with CNT)	285	369	10.8
					ARB 4C (without CNT)	236	337	18.0
(Jamaati <i>et al.</i> , 2018)	2014	Fe	SiC	50 μm	Fe–2 SiC		1323	8.2
				50 nm			1225	9.1

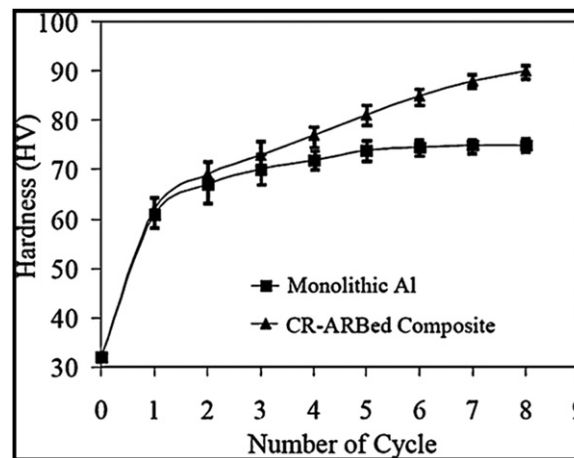


Fig. 17 Variation of microhardness vs. the number of cycles in the CR-ARB Al– B_4C composite and monolithic samples. Reproduced from Alizadeh, M., Paydar, M.H., 2012. High-strength nanostructured Al/ B_4C composite processed by cross-roll accumulative roll bonding. *Materials Science and Engineering A* 538, 14–19.

of the composites. The dislocation motion can be affected by the reinforcement particulates which eventually leads to the mechanical properties, the mechanism playing here is dispersion/Orowan strengthening (Chandrasekar *et al.*, 2009).

- (3) Particle size: Comparing with coarse particles, distribution of fine particulates in the MMCs work as a barrier to the dislocation motion, i.e., retards the movement of grains and grain boundaries and inhibits the grain growth at both room and elevated high temperatures. According to Hall-Petch relation, finer grains can produce a greater number of grains and grain boundaries which impedes the dislocation motion, known as grain refinement strengthening (Chandrasekar *et al.*, 2009).
- (4) Interfacial bonding quality: It is well known in MMCs, the fracture initiates and nucleates further at the interface and link with other crack causes the material to fail at heavy load. Hence, it is required to improve the strength at the interface to make it stronger, which can be done by applying higher rolling pressure during roll bonding in order to enhance the tensile strength and elongation.

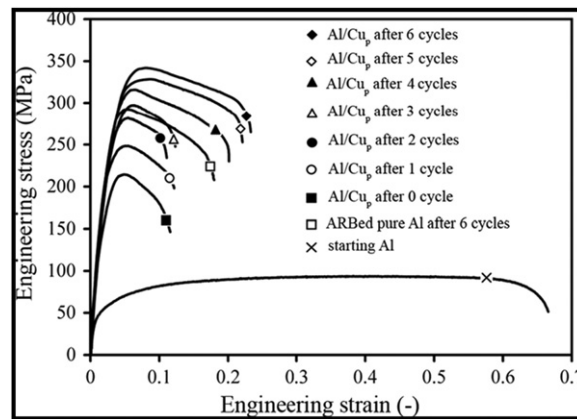


Fig. 18 Engineering stress–strain curves for starting Al, ARBed pure Al after sixth cycle and Al/Cu_p composite within different cycles of ARB process. Reproduced from Alizadeh, M., Talebian, M., 2012. Fabrication of Al/Cu_p composite by accumulative roll bonding process and investigation of mechanical properties. *Materials Science & Engineering A* 558, 331–337.

Table 3 Ultimate tensile strength of Al–SiC composites developed using various technique

Ref.	Process	Matrix	Reinforcement	wt%	UTS (MPa)
(Jamaati <i>et al.</i> , 2012)	ARB	A356	SiC	10	348
(Jamaati <i>et al.</i> , 2012)	CAR	A356	SiC	10	167
(Rozak <i>et al.</i> , 1992)	Stir casting	A356	SiC	10	85
(Amirkhanlou and Niroumand, 2011)	Powder metallurgy	A356	SiC	10	130
(Jamaati <i>et al.</i> , 2011)	Casting followed by ARB	A356	SiC	10	100

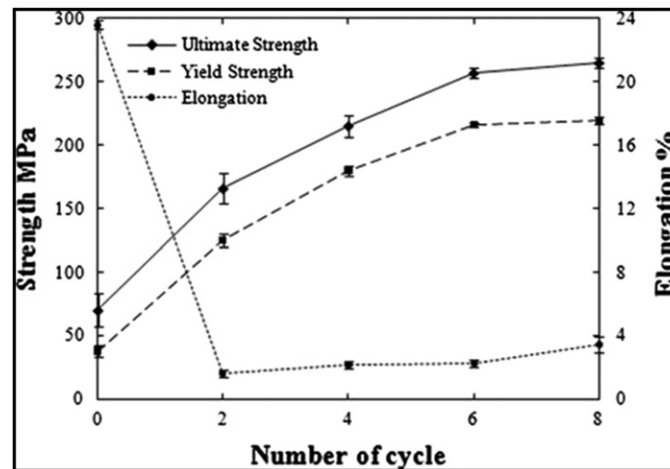


Fig. 19 Mechanical properties of the Al-3.5 vol pct SiC composites produced by the ARB process at various cycle Reproduced from Rezayat, M., Akbarzadeh, A., Owhadi, A., 2012a. Fabrication of high-strength Al/SiC_p nanocomposite sheets by accumulative roll bonding. *Metallurgical and Materials Transactions A* 43, 2085–2093.

- (5) Porosity: Similar to the aforementioned factors, porosity is an influencing factor of the mechanical properties of MMCs. The existence of porosity, either in matrix or at the interface results in the fall of tensile properties. By increasing the ARB cycles, the porosities are eliminated. Therefore, increase in tensile strength and ductility can be achieved.
- (6) Thermal mismatch: During plastic work, frictional heat occurs between the rollers and the composite strips. It is well known that the mismatch of coefficient of thermal expansion (CTE) between matrix and reinforcement will be huge. After ARB, during heat dissipation (cooling), strain is induced in the matrix around the reinforcement particles leading to the generation of dislocations in specimen called dislocation strengthening. This leads to increase in tensile strength and decrease in ductility (Muralidharan *et al.*, 2018).

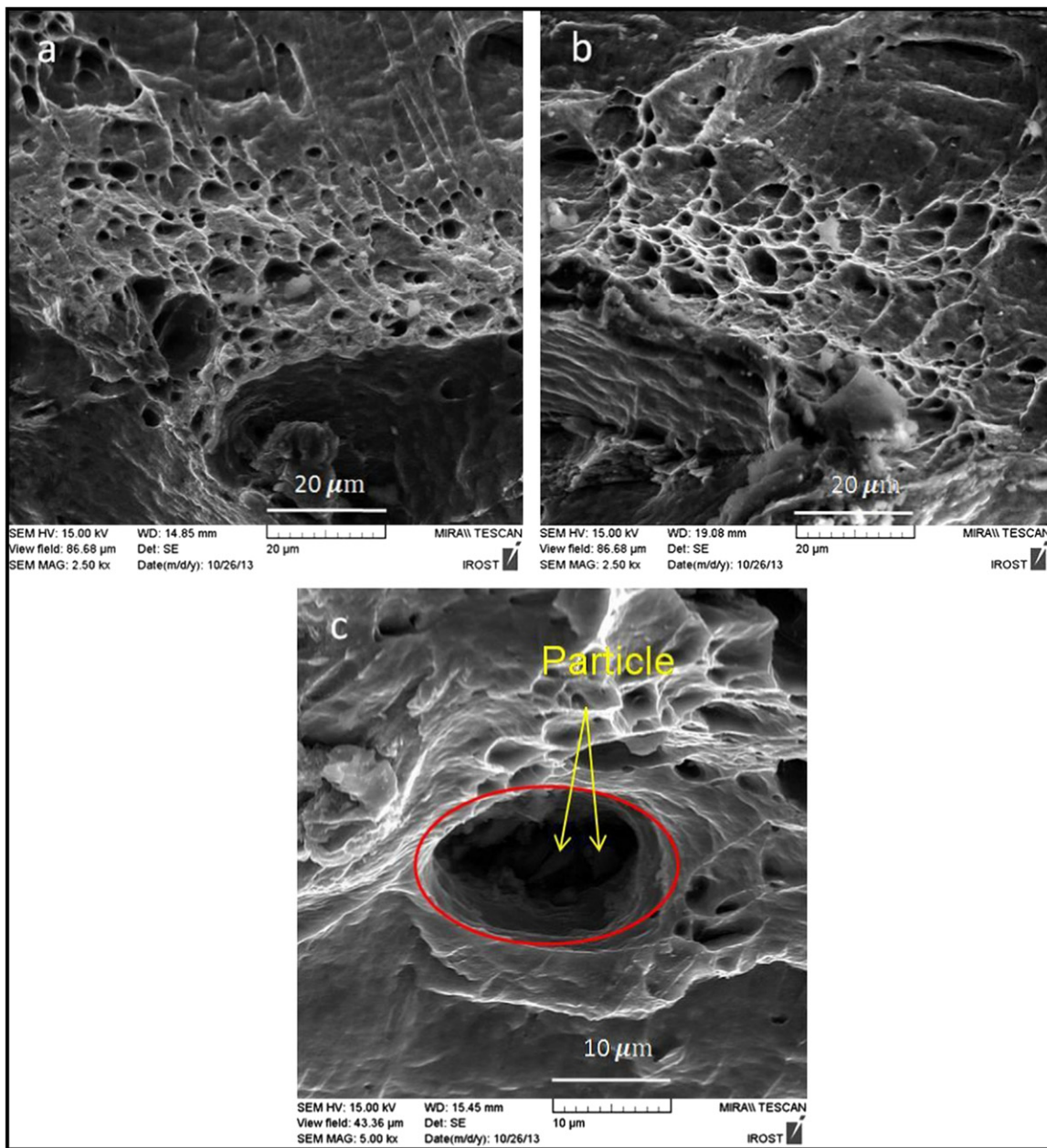


Fig. 20 Tensile fracture surface of (a) annealed Al, (b) monolithic Al and (c) Al/Al₂O₃/SiC hybrid composite after eight ARB cycles. Reproduced from Reihanian, M., Keshavarz Hadadian, F., Paydar, M.H., 2014. Fabrication of Al-2 vol% Al₂O₃/SiC hybrid composite via accumulative roll bonding (ARB): An investigation of the microstructure and mechanical properties. *Materials Science & Engineering A* 607, 188–196.

Fig. 17 depicts the Vicker's microhardness graph of monolithic Al and Al/B₄C MMCs (Rezayat *et al.*, 2012a). The sudden upsurge in hardness values at the initial cycles is due to strain hardening effect, i.e., increase in dislocation density, further slight increase is due to addition of grain refinement owing to the addition of reinforcement particles. **Fig. 18** demonstrates the stress-strain curves of Al-Cu composites by increasing the passes from 0 to 6, for a comparison of pure Al and Al ARB after 6 cycles were considered. By increasing the rolling cycles i.e., strain, the flow stress attains to its ultimate position, also where macroscopic necking is noticed in the curve. It can be understood from **Fig. 19** that there is a sudden increase till sixth cycle followed by saturation in YS and UTS. Because up to third cycle, strain hardening takes place to form subgrains. The dislocation strengthening is slowly reduced with increase in ARB cycles, and the improvement of the properties was due to presence of ultrafine grain with high misorientations. Additionally, another mechanism is the formation of geometrically necessary dislocations around the reinforcement while plastic deformation takes in MMCs. In accordance with this mechanism, the geometrical mismatch will be generated as a result of the deformation-induced plastic strain gradient around the particles in the matrix. It should be noted that due to the variation of temperature during the production process, geometrical dislocations will be generated to accommodate

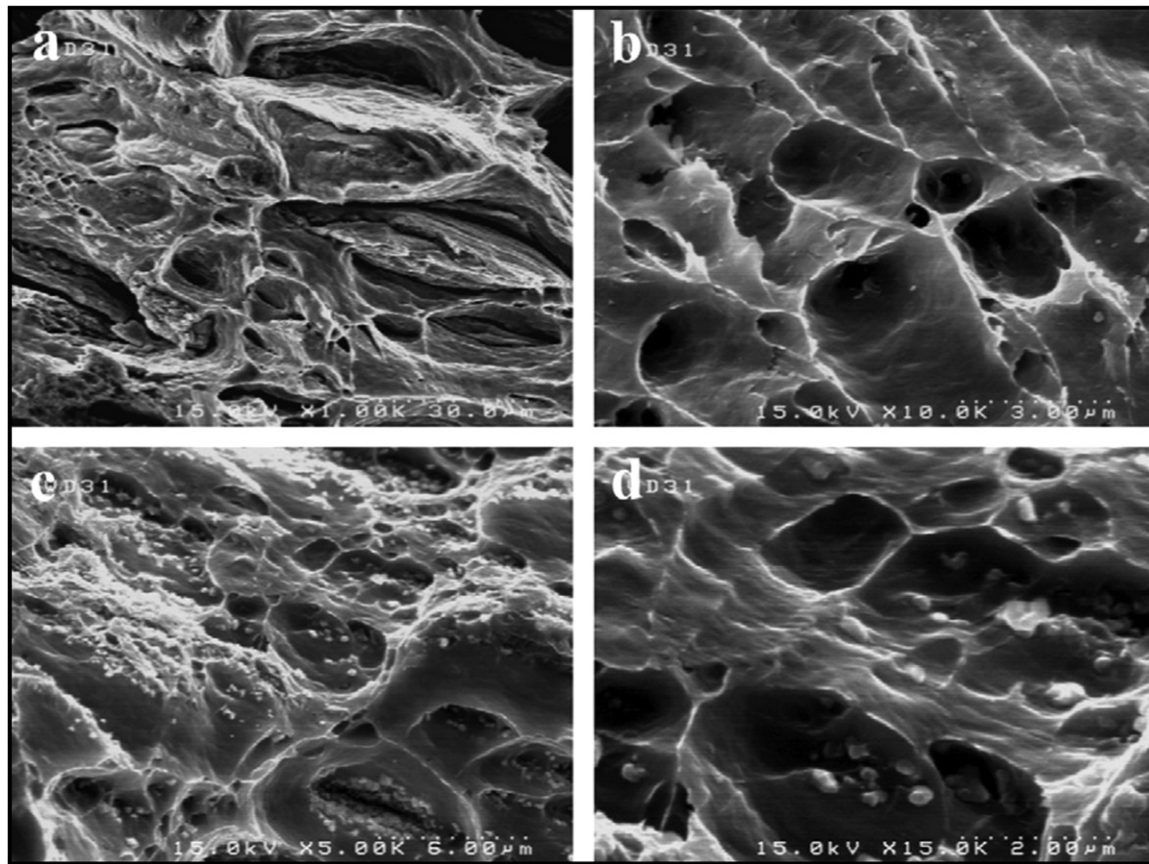


Fig. 21 Fractographs in two magnifications for (a and b) non-reinforced aluminum with 8 ARB cycles, and (c and d) Al-3 vol% Al₂O₃ composite with 8 ARB cycles after tensile test. Reproduced from Rezayat, M., Akbarzadeh, A., Owghadi, A., 2012b. Production of high strength Al-Al₂O₃ composite by accumulative roll bonding. Composites: Part A 43, 261–267.

the strain incompatibility around the particles (Kazemi Talachi *et al.*, 2011). Because of the low rolling temperature, however, the effect of temperature variation on dislocation density is negligible. The presence of more dislocations in the structure and the interaction between them cause a rapid increase in the work hardening of the composite. Also, it is easy to develop the ultrafine grains in the composite sheet as compared to the unreinforced one (Sivasankaran and Alaboodi, 2016; Kieback, 2011).

It is essential to examine the fractured surface after tensile test. This testing method helps to determine the mode of failure in engineering components in service condition. Consistent with shear lag mechanism, load carrying capacity will be higher for coarse particles than fine particles. But coarse particles have more possibility for critical flaw and cracking (Tsuji *et al.*, 2013; Jamaati *et al.*, 2014a). In MMCs, owing to the addition of fine ceramic particles, they can withstand the dislocation motion occurring while applying external load as it possesses high strength. Due to the mismatch between elastic modulus of matrix and reinforcement causes the local stress in the MMCs which leads to particles decohesion at the interface. Indeed, nucleation of voids at interface and their coalescence is the governing fracture mechanism.

Table 3 represents the UTS values obtained from Al-10 wt% SiC reinforced MMCs through ARB, CAR, stir casting, powder metallurgy, and semisolid processing (casting followed by ARB). Among these processes, composite fabricated through stir casting technique show very low tensile strength of 85 MPa followed by semi-solid processing, powder metallurgy, CAR, and ARB in sequence. Their corresponding tensile strength values are 100, 130, 167, and 348 MPa, respectively. The lower value in stir casting was due to porosity, coarser grains, and clustering of particles due to density mismatch between matrix and reinforcement. In order to improve the dispersion of reinforcement, secondary process like ARB was tried to improve the strength, only 100 MPa could be achieved due to delamination and poor bond strength. Another method of solid-state processing such as powder metallurgy was tried in the same system, which can provide 130 MPa, still it could be better. In P/M process, porosity is the difficult task to nullify even after sintering. Finally, CAR and ARB are the techniques to overcome the shortcomings faced by other processes. Using CAR, maximum tensile strength of 167 MPa could be obtained. Though it is reasonable, does not provide huge strength than other processes. Oxidation is the foremost problem occurring during CAR process which makes the specimen to delaminate. Finally, in ARB process, the maximum tensile strength of 348 could be achieved after several passes. At last, the specimen was defect free like non-porous, proper distribution of reinforcements, ultra-fine grains and strong layer to layer bonding.

Fig. 20 reveals the fracture behavior of the monolithic and annealed Al with hybrid composites (Reihanian *et al.*, 2014). Equiaxed and finer dimples are observed in annealed and monolithic Al specimens (**Fig. 9(a)** and **(b)**). In particular, some dimples are elongated in one or other direction owing to unequal triaxial stresses. The examined fracture shows the appearances of typical ductile fracture. Very close dimples in monolithic Al shows very lower amount of Al matrix existing between them due to work hardening and lower ability for plastic work. In hybrid composite, initiation and growth of void at the interface in hybrid composite is shown in **Fig. 20(c)**. The dimples that are nucleated at the particle sites are considerably deeper and larger than that initiated at other locations. The particles responsible for the void nucleation can be observed at the bottom of these dimples. The size, separation, and interfacial bonding of these particles decides the nature of fracture corresponding to ductile behavior. The reduction in elongation of the composite can be due to extensive void nucleation and link up other voids.

The fractography (Rezayat *et al.*, 2012b) of unreinforced and Al₂O₃ reinforced Al composite after 8 cycles of ARB are illustrated in **Fig. 21**. The fracture occurred in both the specimens by matrix ductile rupture mechanism. Shear ductile rupture is the one mode of fracture in unreinforced matrix which has been identified through gray fibrous with dimples. Deep and elongated dimples are the results of nucleation of micro voids, their growth and finally coalescence of dimples which are affected by shear stress. Whilst from **Fig. 21(c)** and **(d)**, it can be clearly observed that the presence of second phase particles and its substantial influence on the fracture surface. The fracture initiated at the interface which has been ensured through the presence of particulates in the inner core of dimples. Furthermore, dimples in Al–Al₂O₃ composite are small and shallow when compared with unreinforced matrix, which are the reflection of their respective grain size (**Fig. 21(d)**).

Summary and Future Outlook

The advantages of ARB process are as follows: (1) Isotropic behavior, (2) production of ultrafine/nano-grained bulk material, (3) maximum strain rate super plastic behavior, (4) does not require expensive forming tools, (5) cost effective technique, (6) uniformity in the entire surface, (7) reduction of porosity level, (8) absence of gas entrapment, (9) mass production is possible, (10) high load capacity forming facilities, expensive dies are not needed, (11) productivity rate is high, and (12) the amount of material to be produced is not limited. Hence, ARB can be considered as a promising technique to solve the issues occurring in other composite fabrication process such as casting, P/M and FSP.

Whereas the limitations in ARB process are: (1) Loss of ductility, (2) difficulty in dispersion for higher volume fraction, (3) optimization of process parameters (roll speed, load), (4) excess load and roll speed delaminate the strips, and (5) edge cracking.

Additional application of the ARB process in the near future is to produce metal matrix composite electrodes for joining monolithic alloys and metal matrix composites by fusion welding techniques (Ramkumar and Natarajan, 2018; Fattahi *et al.*, 2015). A composite electrode is advantageous to increase the strength of the joint as it introduces more particles into the weld pool. The uniform distribution of ARB composite will provide better dispersion of reinforcement particles in the fusion zone which is beneficial. Few works were reported on manufacturing MMCs based on steel and titanium using ARB. ARB process is to developed which will be beneficial to produce thin composite strips for aero space and other components operating at higher temperature.

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Friction Stir Processing Route for Metallic Matrix Composite Production

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Introduction

Metal matrix composites (MMCs) have become one of the important class of engineering materials of the modern era. MMCs have drawn a huge research focus in recent years. MMCs were initially conceived during the 1960s but the advancement of production technologies made it possible to manufacture various combination of matrix and reinforcements. Particles of various materials are currently used as reinforcement for MMCs. The size of particles varies from micron to nano levels. Ceramic and carbonaceous particles remain a popular choice. MMCs are characterized by many desirable properties and features such as low weight, high specific strength, superior wear resistance, limited thermal expansion, high temperature stability, improved resistance to creep, etc. Therefore, MMCs are most sought after in several industries to substitute components produced using conventional monolithic alloys. MMCs help to improve the performance of industrial components without invoking additional weight into the system (Miracle, 2005; Sidhu *et al.*, 2016; Lloyd, 1994; Kaczmar *et al.*, 2000).

MMCs are produced by combining a matrix material and a reinforcement. This presents lot of challenges to successfully manufacture MMCs. The final MMCs product should have a homogenous distribution of the reinforcement phase to enhance the properties and component service life. Liquid metallurgy routes are commonly used to make MMCs because of simplicity, applicability to mass production, and economic reasons. The chosen matrix material is melted in the beginning of the process and the selected reinforcement particles are fed to the molten metal. Although the description of the process looks simple, it involves several hurdles. Most of the ceramic particles do not wet the molten metal causing rejection from the melt. The density gradient causes either upward or downward movement which results in settling or floating. Further, the higher temperature initiates interfacial reaction between the molten metal and the reinforcement particle producing undesirable brittle intermetallic particles. The solidification pattern influences the distribution of particles adversely. Several methods are used to improve the issues with wettability and other setbacks (Taha, 2001; Hashim *et al.*, 1999, 2002; Yigezu *et al.*, 2013; Ravi *et al.*, 2007; Hashim *et al.*, 2001). A solid-state method is highly preferred to overcome those limitations.

Friction Stir Processing

Friction stir processing (FSP) has evolved as a potential solid-state method to produce surface and bulk MMCs effectively. FSP was conceived from the latest solid-state welding technology namely friction stir welding (FSW) which was invented at The Welding Institute in 1991. Mishra *et al.* (2003) first published an article to prepare MMCs using FSP. The method is relatively simple. The working principle can be visualized in Fig. 1 (Lee *et al.*, 2006). The matrix material is usually taken in the form of plate which may be in extruded or rolled form. A groove is machined on the top of the plate in order to accommodate the reinforcement particles. The size of the groove is chosen based on the volume fraction and the depth of processing required. A milling machine or wire electric discharge machine can be used to cut the groove. The particles are then stuffed into the groove manually or pre pressed powders can be packed into the groove. The opening of the groove at the top leads to escape of particles during processing. This can be avoided by processing using a pinless tool initially. The pinless tool plasticizes a thin layer of material and moves from one side to another and closes the groove opening. Subsequent processing is carried out using a conventional FSW tool. The tool is not consumed and has two parts namely shoulder and pin. The rubbing of tool shoulder and shearing action of the pin generate frictional heat which causes plasticization of the material. The geometry and the material of the tool determines the quantity of frictional heat generated and subsequently the degree of plasticization. The rotary and transverse movement of the tool causes material flow from advancing side to retreating side. The stirring action of the tool mixes the packed particles into the plasticized material and creates the composite which is consolidated at the back of the tool due to the application of axial force on the tool. The temperature raise is above the recrystallization temperature of the substrate material and insufficient to melt the matrix material. The whole processing of making the composite is accomplished in solid state (Ma, 2008; Arora *et al.*, 2012; Sharma *et al.*, 2015; Bajakke *et al.*, 2019; Ratheea *et al.*, 2018).

There are various strategies adopted to fabricate the composite as depicted in Fig. 2. Groove strategy is most common. The cross section of the groove may be square, rectangle or V shaped (Liu *et al.*, 2013; Avettand-Fènoël *et al.*, 2014). The volume fraction is maximum in square groove compared to V groove. If the tool does not provide sufficient vertical flow of material, a V groove may lead to functionally graded distribution along the depth. A cover sheet is sometimes used to avoid scattering of particles in lieu of pinless tool. The thickness of the cover plate is crucial to successfully plasticize and mix with the particles in the groove. A thicker cover plate may lead to debonding at the edges of the groove and cause hook defect. Some investigators used an array of drilled holes instead of grooves to pack reinforcement particles. There is a gap between holes in the array. Multiple columns were also

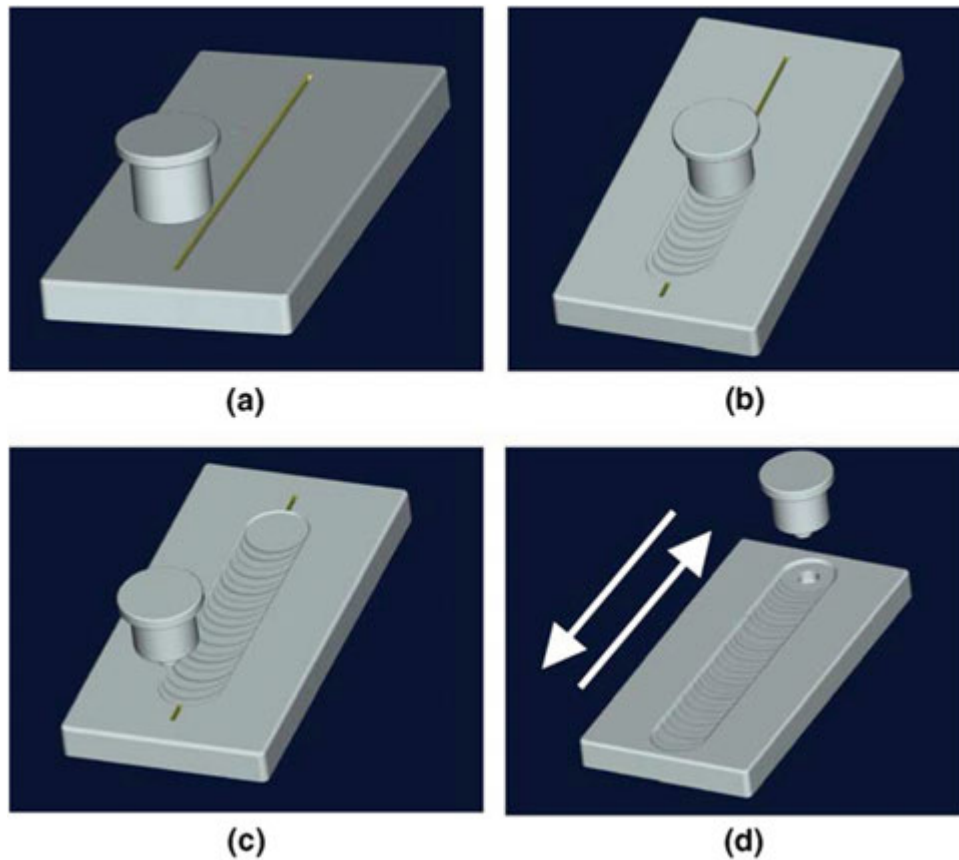


Fig. 1 The FSP procedure: (a) cutting groove(s) and inserting particles; (b) using a flat tool to undertake the surface repair; (c) applying a tool with a fixed pin to undertake the FSP; and (d) conducting multiple FSP passes. Reproduced from Lee, C.J., Huang, J.C., Hsieh, P.J., 2006. Mg based nano-composites fabricated by friction stir processing. *Scripta Materialia* 54, 1415–1420.

used in few investigations. This arrangement may avoid the need for a cover sheet or a pinless tool and reduce the processing time. However, the distribution will not be constant along the FSP track. The volume fraction is high at the location of holes and low between the hole location. In all these methods, the depth of the groove or the hole determines the depth of the particle rich processing zone. It is possible to increase the depth of processing by increasing the length of tool pin considerably to groove depth at the cost of deprived distribution. Another strategy is to precoat the plate with the reinforcement particle and do the processing. The precoating can be done by mixing reinforcement with a solvent and apply using a brush. This method produces surface composites to a lower thickness of less than 1 mm (Ratna Sunil, 2016).

FSP process is attractive and presents many benefits. It does not consume huge amount of energy compared to liquid metallurgy methods. The physical and chemical properties of the reinforcement particles have little or no influence on the nature of the process. The density gradient or the wettability do not play a role in determining the final dispersion of the particles in the composite. Therefore, the options of reinforcement using FSP is unlimited. Practically, any potential particle can be reinforcement with ease. The processing temperature does not promote undesirable interfacial reactions between the matrix and the reinforcement. Absence of solidification avoids unnecessary pushing of particles during consolidation (Zohoor *et al.*, 2012; Kurta *et al.*, 2011; Yuvaraj *et al.*, 2017; Shyam Kumar *et al.*, 2015; Akramifard *et al.*, 2014).

Microstructural Features

The common microstructural features of MMCs produced using FSP are presented in this section. FSP was successfully applied to produce composites based on aluminum, magnesium, copper, steel, and titanium as matrix materials. FSP produces a stir zone similar to FSW. The stir zone houses the composite. Typical appearance of stir zone of various composites is presented in Fig. 3. It is essential to obtain a stir zone without any macroscopic defects such as pin hole, worm hole, tunnels, and irregular voids. Optimization of process parameters is necessary to obtain a sound stir zone. Nevertheless, a defect free stir zone does not guarantee proper dispersion of reinforcement particle. Grains adjacent to stir zone may undergo coarsening due to frictional heat and constitute heat affected zone (HAZ). However, the size of HAZ is less to that of conventional FSW because the reinforcements absorb heat and act as heat sink.

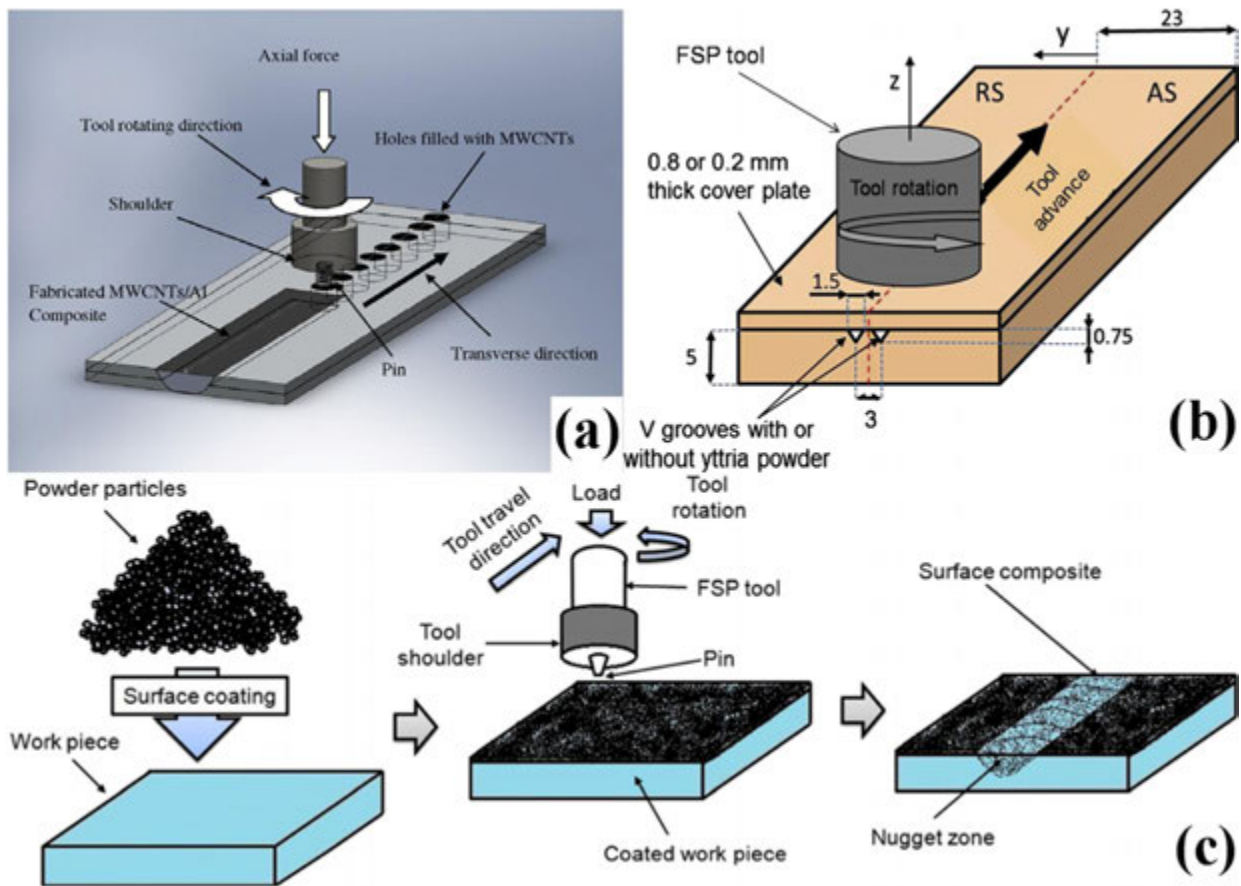


Fig. 2 Strategies to reinforce the particles using FSP: (a) array of holes, (b) V groove and cover plate, and (c) precoated particles. Reproduced from Liu, Q., Ke, L., Liu, F., Huang, C., Xing, L., 2013. Microstructure and mechanical property of multi-walled carbon nanotubes reinforced aluminum matrix composites fabricated by friction stir processing *Materials and Design* 45, 343–348. Avettand-Fènoël, M.N., Simar, A., Shabadi, R., Taillard, R., De Meester, B., 2014. Characterization of oxide dispersion strengthened copper based materials developed by friction stir processing. *Materials and Design* 60, 343–357. Ratna Sunil, B., 2016. Different strategies of secondary phase incorporation into metallic sheets by friction stir processing in developing surface composites. *International Journal of Mechanical and Materials Engineering* 11, 12.

Aluminum Matrix Composites

FSP was initially applied to aluminum alloys to make composites before extending to other nonferrous and ferrous materials. Aluminum and its alloys can be plasticized with ease compared to other materials. An overview of various aluminum composites by FSP technique is presented in [Table 1](#). Several kind of reinforcement particles including SiC ([Ghanbari et al., 2017](#); [Rathee et al., 2017](#); [Wang et al., 2009](#)), Al_2O_3 ([Mazaheri et al., 2011](#); [Zarghani et al., 2009](#)), TiC ([Thangarasu et al., 2015](#)), B_4C ([Rana and Badheka, 2018](#); [Zhao et al., 2015](#)), WC ([Huang et al., 2018](#)), TiB_2 ([Palanivel et al., 2016](#)), TiO_2 ([Khodabakhshi et al., 2014](#); [Joyson Abraham et al., 2019](#)), ZrO_2 ([Mirjavadi et al., 2017](#)), SiO_2 ([Joyson Abraham et al., 2016](#)), fly ash ([Dinaharan et al., 2016b](#)), rice husk ash ([Dinaharan et al., 2017b](#)), CNT ([Lim et al., 2009](#); [Hosseini et al., 2015](#)), graphene ([Maurya et al., 2016](#); [Sharma et al., 2019](#)), graphite ([Mostafapour Asl and Khandani, 2013](#)), NiTi ([Dixit et al., 2007](#); [Ni et al., 2014](#)), W ([Bauri et al., 2015](#)), Ti ([Huang and Shen, 2017](#)), Ni ([Yadav and Bauri, 2011](#)), Mo ([Selvakumar et al., 2017a](#)), SS ([Selvakumar et al., 2017b](#)), Cu ([Yadav and Bauri, 2015](#)), and fibers ([Arab et al., 2015](#)) were successfully used to produce the composites. Such a variety of reinforcements cannot be tried using conventional stir casting methods. FSP is flexible enough to reinforce any kind of particle irrespective of its physical and chemical properties. A reasonable distribution and an improvement of properties were reported in most of the literature.

[Dinaharan \(2016\)](#) fabricated AA6082 based AMCs by reinforcing several ceramic particles such as SiC, Al_2O_3 , TiC, B_4C , and WC and investigated the microstructural features and the response of FSP process to fabricate variety of composites. [Fig. 4](#) shows SEM micrographs of AA6082 AMCs which clearly reveal the distribution of ceramic particles in the aluminum matrix. The distribution of ceramic particles is observed to be fairly homogeneous. There are no clusters or agglomeration of particles seen. Moreover, there is no segregation of particles along the grain boundaries. Some particles might be located on the grain boundaries due to smaller grain size. But entrapment of particles within grain boundaries is absent. Hence, the distribution is considered to be roughly intragranular. The mechanical and tribological properties of AMCs are influenced by the nature of distribution. A homogeneous and intragranular distribution is essential to attain higher properties. The FSP process has resulted in the desirable dispersion. Stir

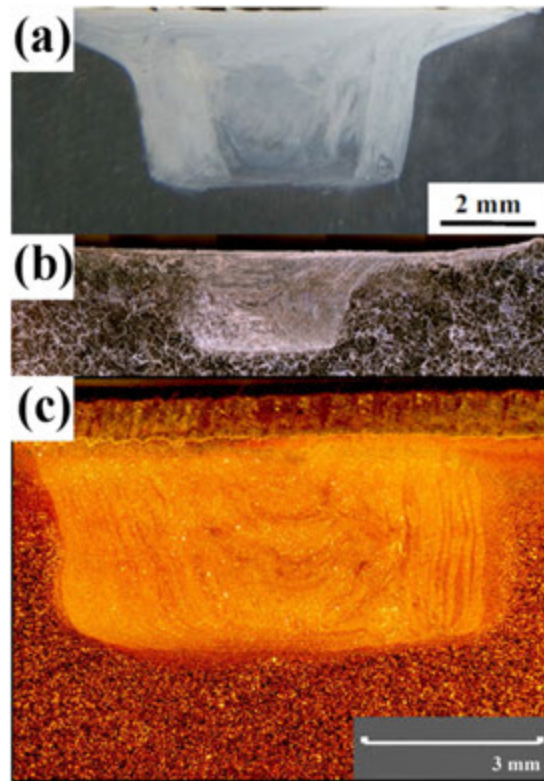


Fig. 3 Optical macrostructure of stir zone containing: (a) AA5083/WC; (b) AZ91/ Al_2O_3 ; and (c) Cu/ TiB_2 . Reproduced from Huang, G., Hou, W., Shen, Y., 2018. Evaluation of the microstructure and mechanical properties of WC particle reinforced aluminum matrix composites fabricated by friction stir processing. *Materials Characterization* 138, 26–37. Faraji, G., Asadi, P., 2011. Characterization of AZ91/alumina nanocomposite produced by FSP. *Materials Science and Engineering A* 528, 2431–2440. Dinaharan, I., Saravanakumar, S., Kalaiselvan, K., Gopalakrishnan, S., 2017c. Microstructure and sliding wear characterization of Cu/ TiB_2 copper matrix composites fabricated via friction stir processing. *Journal of Asian Ceramic Societies* 5, 295–303.

Table 1 Aluminum matrix composites fabricated by friction stir processing

Matrix	Reinforcement	Size	Reference
AA2024-T351	SiC	50 nm	(Ghanbari <i>et al.</i> , 2017)
AA6063-T6	SiC	10 μm	(Rathee <i>et al.</i> , 2017)
A356	Al_2O_3	50–100 μm , 20–40 nm	(Mazaheri <i>et al.</i> , 2011)
AA6082	TiC	2 μm	(Thangarasu <i>et al.</i> , 2015)
AA7075	B_4C	8–12 μm , 15–18 μm	(Rana and Badheka, 2018)
AA5083	WC	27 μm	(Huang <i>et al.</i> , 2018)
AA6082	TiB_2	20 μm	(Palanivel <i>et al.</i> , 2016)
Al–Mg	TiO_2	30 nm	(Khodabakhshi <i>et al.</i> , 2014)
AA5083	ZrO_2	110 nm	(Mirjavadi <i>et al.</i> , 2017)
AA6063-T6	SiO_2	32 μm	(Joyson Abraham <i>et al.</i> , 2016)
AA6061	Fly ash	2 μm	(Dinaharan <i>et al.</i> , 2016b)
AA6061	Rice husk ash	8 μm	(Dinaharan <i>et al.</i> , 2017b)
Al 6111–T4/Al 7075–T6	CNT	30–50 nm	(Lim <i>et al.</i> , 2009)
AA6061	Graphene	15 nm	(Maurya <i>et al.</i> , 2016)
AA5083	Graphite	10–50 nm	(Mostafapour Asl and Khandani, 2013)
AA1100	NiTi	2–193 μm	(Dixit <i>et al.</i> , 2007)
AA5083	W	10 μm	(Bauri <i>et al.</i> , 2015)
AA5083	Ti	23 μm	(Huang and Shen, 2017)
AA1050	Ni	70 μm	(Yadav and Bauri, 2011)
AA6082	Mo	25 μm	(Selvakumar <i>et al.</i> , 2017a)
AA6082	SS	40 μm	(Selvakumar <i>et al.</i> , 2017b)
AA1100	Glass fiber	300 μm	(Arab <i>et al.</i> , 2015)

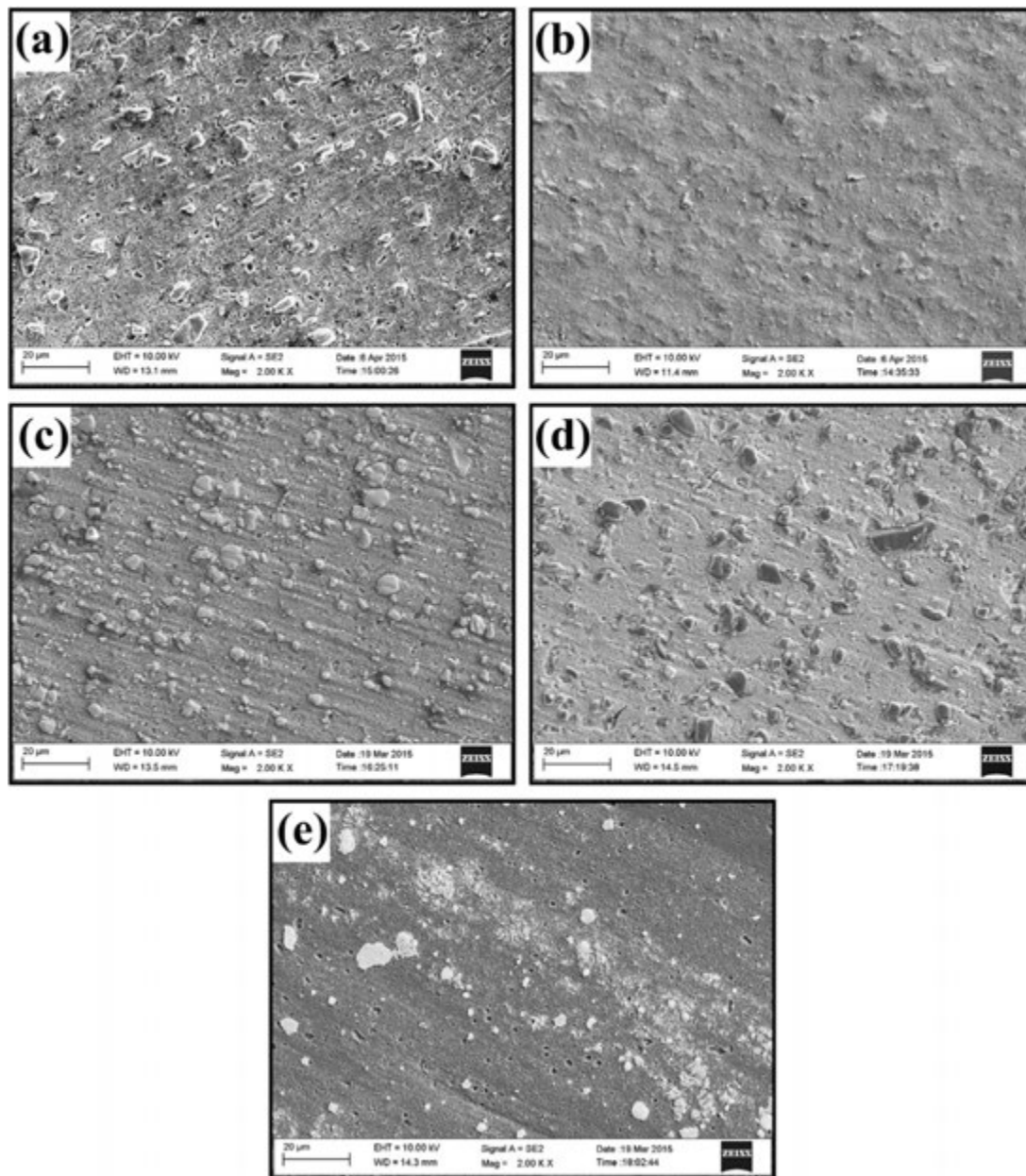


Fig. 4 FESEM micrographs of AA6082 MMCs reinforced with (a) SiC, (b) Al_2O_3 , (c) TiC, (d) B_4C , and (e) WC. Reproduced from Dinaharan, I., 2016. Influence of ceramic particulate type on microstructure and tensile strength of aluminum matrix composites produced using friction stir processing. *Journal of Asian Ceramic Societies* 4, 209–218.

casting technique frequently produce inhomogeneous and intergranular dispersion owing to solidification related phenomena. The density gradient results in improper dispersion (Hashim *et al.*, 2002). Since the aluminum matrix does not melt during FSP, density gradient does not cause free movement of ceramic particles. This leads to proper dispersion. The dispersion of ceramic particles is a function of process parameters such as tool rotational speed and traverse speed (Sharma *et al.*, 2015). A fine and homogeneous distribution in the SEM micrographs confirms that the chosen set of process parameters was sufficient to produce the desirable distribution. The compacted ceramic particles are distributed throughout the stir zone.

FSP induced a change in the size and morphology of ceramic particles. The severe plastic deformation together with the rotating action of the tool is able to smash the ceramic particles. The strong stirring action of the tool knocks off the sharp corners of the ceramic particle. Large size variation of ceramic particles (SiC, TiC, B_4C , and WC) in Fig. 4 indicates the fragmentation. Fragmentation was observed by many researchers (Sharma *et al.*, 2015; Ratheea *et al.*, 2018). The rate of fragmentation depends upon the initial size and shape of the particles. Large size particles and irregular or polygonal shape particles have the tendency to break off during FSP. The retention of shape and size of smaller Al_2O_3 particles after FSP which did not undergo much fragmentation

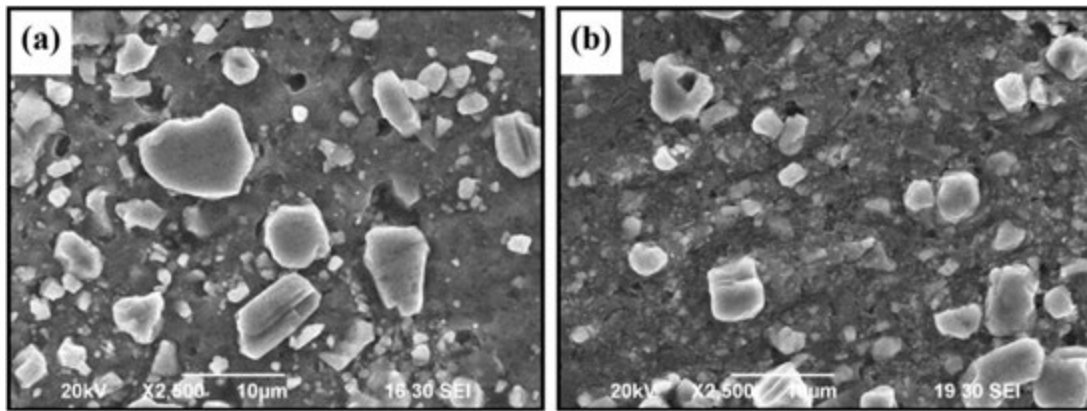


Fig. 5 SEM micrograph of AA6082/TiC MMCs at higher magnification containing: (a) 18 vol%, and (b) 24 vol%. Reproduced from Thangarasu, A., Murugan, N., Dinaharan, I., Vijay, S.J., 2015. Synthesis and characterization of titanium carbide particulate reinforced AA6082 aluminum alloy composites via friction stir processing. *Archives of Civil and Mechanical Engineering* 15, 324–334.

confirms this statement. It is observed that the large ceramic particles are not surrounded by debris generated due to fragmentation. There is no clustering of small debris either. This suggests that the debris also mixed well with the plasticized aluminum and dispersed homogeneously in the aluminum matrix. The size of debris is remarkably low in the order of nanometer compared to the size of initially packed ceramic particles. The size variation leads to functionally graded local areas within the AMC.

Thangarasu *et al.* (2015) presented some details on the interface in AA6082/TiC composites. The details of the interface between the TiC particles and the aluminum matrix can be observed at higher magnification provided in SEM micrographs in Fig. 5. It is observed from the figure that the interface is very clear without the presence of any reaction products or micro pores. A clean interface increases the load bearing capacity of the MMC. The plasticized aluminum matrix might have wetted or spread over the entire surface of the TiC particles during mixing, which may avoid the formation of micro pores. The temperature of the process plays a key role to initiate any kind of reaction between the TiC particle and the matrix. The local temperature developed during FSP is very low compared to liquid metallurgy routes to initiate interfacial reaction.

Palanivel *et al.* (2016) recorded optical photo micrographs of AA6082/TiB₂ aluminum composites at different regions within the stir zone as presented in Fig. 6. TiB₂ particles are dispersed effectively to all regions of the stir zone. There is no region without the dispersion of particles. The distribution is nearly constant across the stir zone. The variation in the dispersion of TiB₂ particles from the advancing side to the retreating side or from the top to the bottom side is small. This led to a conclusion that the distribution is independent of the region in the stir zone. Certain researchers have, however, noticed substantial variation in the dispersion of ceramic particles within the stir zone (Sharma *et al.*, 2015). These distribution variations are the results of insufficient plasticization of the aluminum matrix and non-optimum tool rotational speeds which does not facilitate an even dispersion of the TiB₂ particles to all regions of the stir zone. It is difficult to obtain constant dispersion of ceramic particles across the whole composite synthesized using casting techniques. The velocity of the solidification front will be varying across the mold which induces substantial variation of reinforcement particles across the composite castings.

Selvakumar *et al.* (2017a) elaborated the grain size evolution in AA6082/Mo composites. EBSD images of the AA6082/Mo MMCs and the effect of Mo particles on the grain size are presented in Fig. 7. The grain structure present in the composites is clearly revealed in the EBSD images. The grain structure of the aluminum matrix exhibits a combination of coarse elongated grains and fine grains. The evolution of elongated grain structure is due to rolling process of the as-received aluminum plates. The average grain size was 31.66 µm. The grains in the composite show (Fig. 7(b–d)) very fine and equiaxed structure. The grains are refined extensively in the composite. It is well documented in the literature that dynamic recrystallization during FSP results in the formation of fine-grained structure (Ma, 2008). Metals which undergo hot working processes encounter dynamic recrystallization. Recrystallization takes place due to severe plastic deformation and frictional heating. Dynamic recrystallization is accomplished in the following ways: (a) continuous extended recovery processes through extinction and rearrangement of dislocations and (b) discontinuous formation of relatively dislocation free grains through recrystallization (Emami and Saeid, 2015). The mechanism of operation is depended upon the strain rate history in addition to stacking fault energy of the material. Since aluminum possesses high stacking fault energy, it undergoes continuous dynamic recrystallization. It is observed in Fig. 7(b–d) that the grain size decreased with an increase in Mo particle volume fraction. This observation suggests that Mo particles might acted as grain refiners. Mo particles pinned the movement of grain boundaries which reduced the rate of grain growth. This pinning effect leads to refinement of grains. It is interesting to note that the average particle size of Mo particles is several times higher than the average grain size in the composite. Although porous Mo particles broke during FSP, several large size particles were retained in the composite. A large Mo particle can neither be retained within the grains nor between adjacent grain boundaries. Hence, a large particle may be covering several grains. The grain size reduction is drastic from 0 vol% to 6 vol% and gradual from 6 vol% to 18 vol%. This result is contrary to the trend observed in MMCs using liquid metallurgy techniques and can be related to the nature of FSP. A reinforcement particle acts as a grain nucleating site within the solidifying composite which restricts the grain growth of

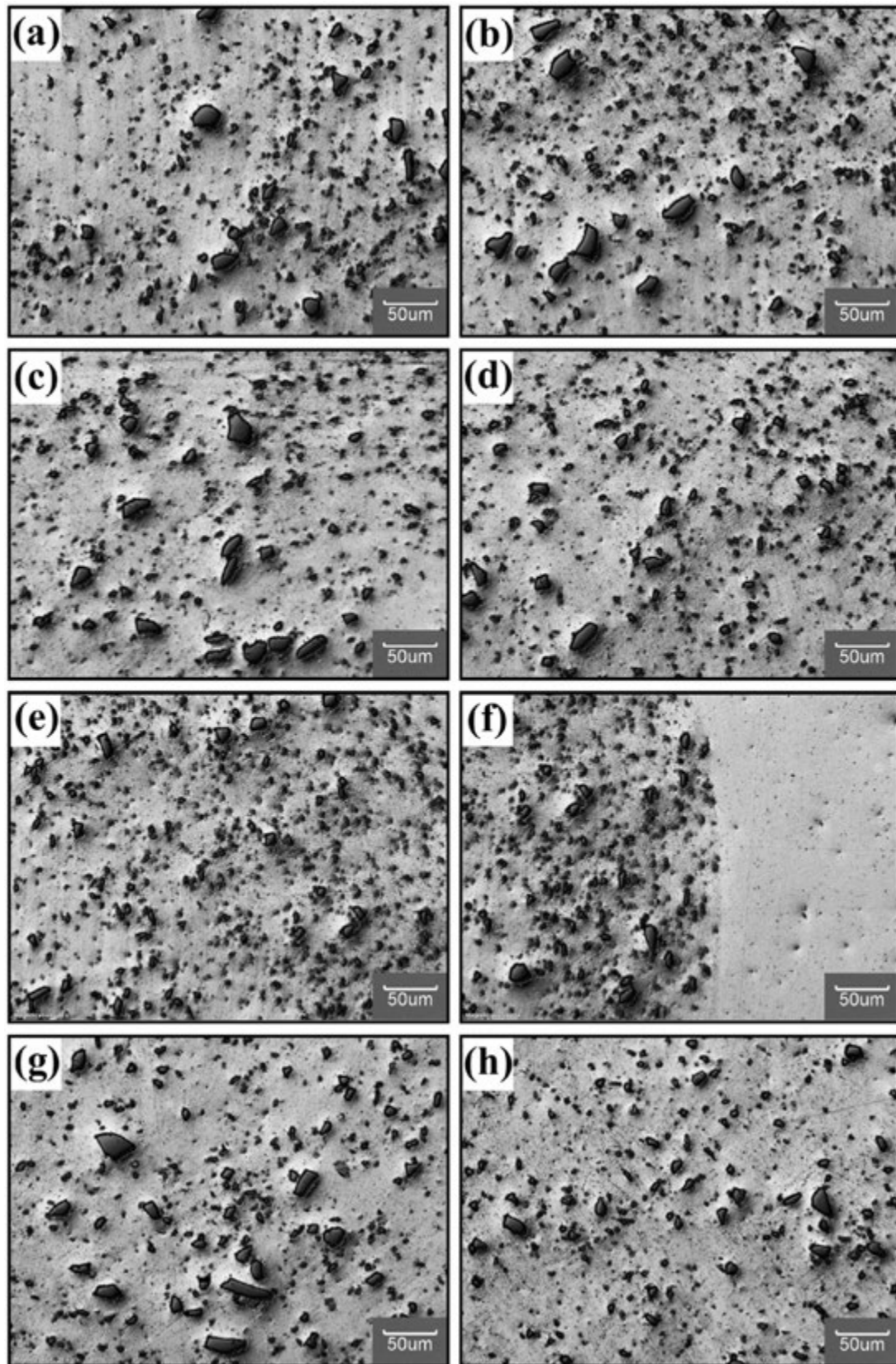


Fig. 6 Optical photomicrograph of AA6082/TiB₂ MMCs at various locations within the stir zone: (a) and (b) toward advancing side, (c) and (d) toward retreading side, (e) middle portion, (f) interface between stir zone and aluminum matrix, (g) and (h) bottom portion. Reproduced from Palanivel, R., Dinaharan, I., Laubscher, R.F., Paulo Davim, J., 2016. Influence of boron nitride nano particles on microstructure and sliding wear behavior of AA6082/TiB₂ hybrid aluminum matrix composites synthesized by friction stir processing. *Materials and Design* 106, 195–204.

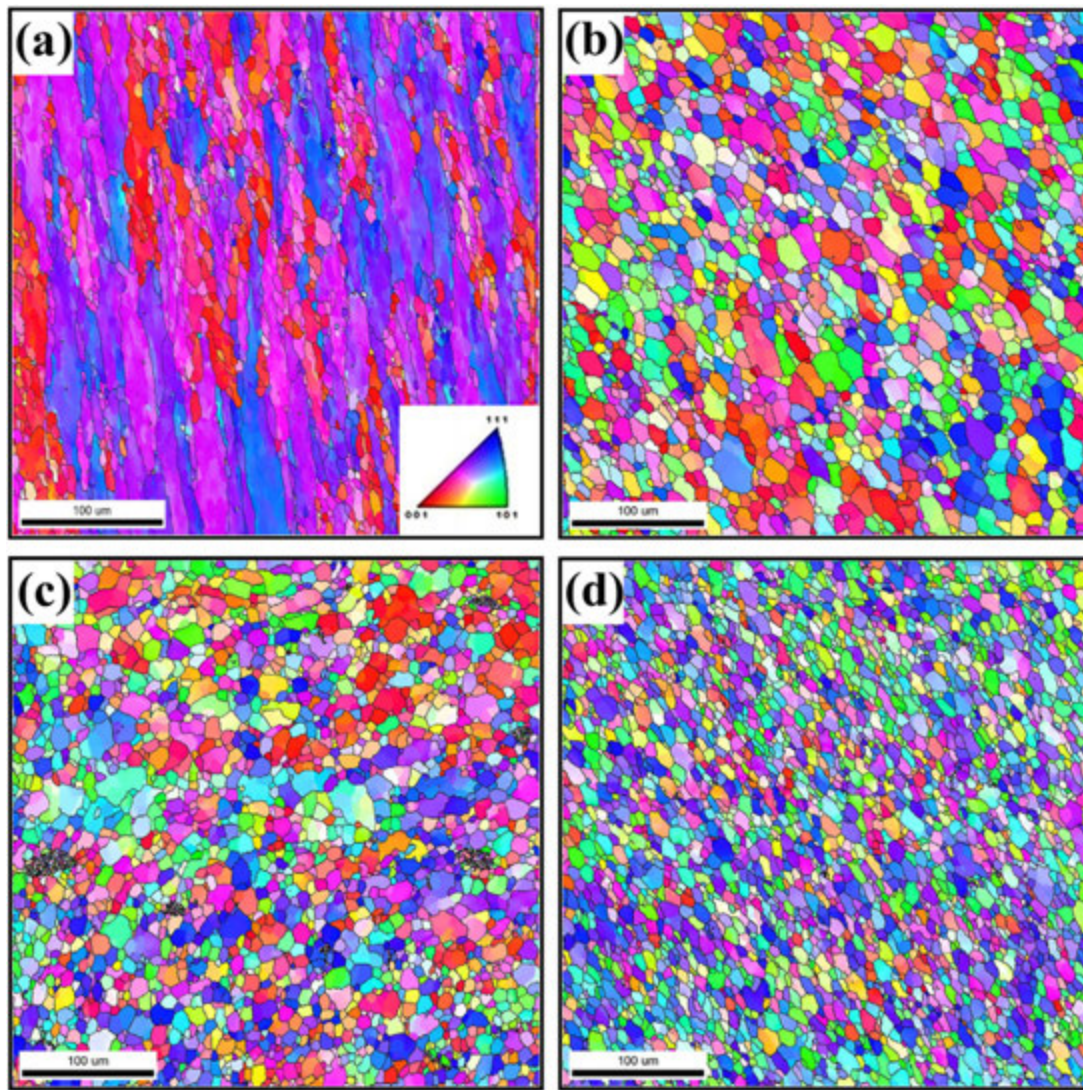


Fig. 7 EBSD (IPF + grain boundary) maps of AA6082/Mo AMCs containing Mo particles: (a) 0 vol% (b) 6 vol%, (c) 12 vol%, and (d) 18 vol%. Reproduced from Selvakumar, S., Dinaharan, I., Palanivel, R., Ganesh Babu, B., 2017a. Characterization of molybdenum particles reinforced Al6082 aluminum matrix composites with improved ductility produced using friction stir processing. *Materials Characterization* 125, 13–22.

aluminum. Hence, a uniform reduction in grain size with increased content of homogeneously distributed reinforcement particles can be expected. Conversely, FSP technique employs an additional mechanism due to intense plastic deformation which negates the pinning effect.

Bauri *et al.* (2015) recorded microstructural features of AA5083/W MMC using TEM as depicted in Fig. 8. Fine equiaxed grains are visible in Fig. 8(a). The particle–matrix interface is presented in Fig. 8(b). The interface is sharp and free from intermetallics or any other reaction products. Fine grains are formed by the dynamic recrystallization as discussed earlier. The high stacking fault energy of Al leads to rearrangement of dislocations into sub-grain boundaries by dynamic recovery (DRV). TEM observations show that dislocations are in the process of rearrangement into sub-grain boundaries (Fig. 8(c)). A magnified image of the sub-grain boundary in Fig. 8(d) shows that the sub-grain boundary is indeed composed of a well-arranged array of dislocations. Incorporation of dislocations, generated during the deformation process, into the sub-grain boundaries gradually increases the misorientation and they progressively turn into low-angle grain boundaries. The diffraction contrast observed between many of the sub-grain boundaries (Fig. 8(e)) in TEM also confirms that misorientation across these boundaries is close to high angle. Dislocation glide assisted lattice rotation may turn these boundaries into high-angle grain boundaries producing a recrystallized fine-grained structure. It is known that continuous dynamic recrystallization (CDRX) takes place by gradual transformation of low-angle sub-grain boundaries, formed by dislocation rearrangement, to high-angle boundaries. Therefore, it appears that a continuous type dynamic recrystallization process driven by dynamic recovery (DRV) has resulted in the fine-grained structure. The basic mechanism of grain structure evolution is not changed due to the nature of reinforcement particle.

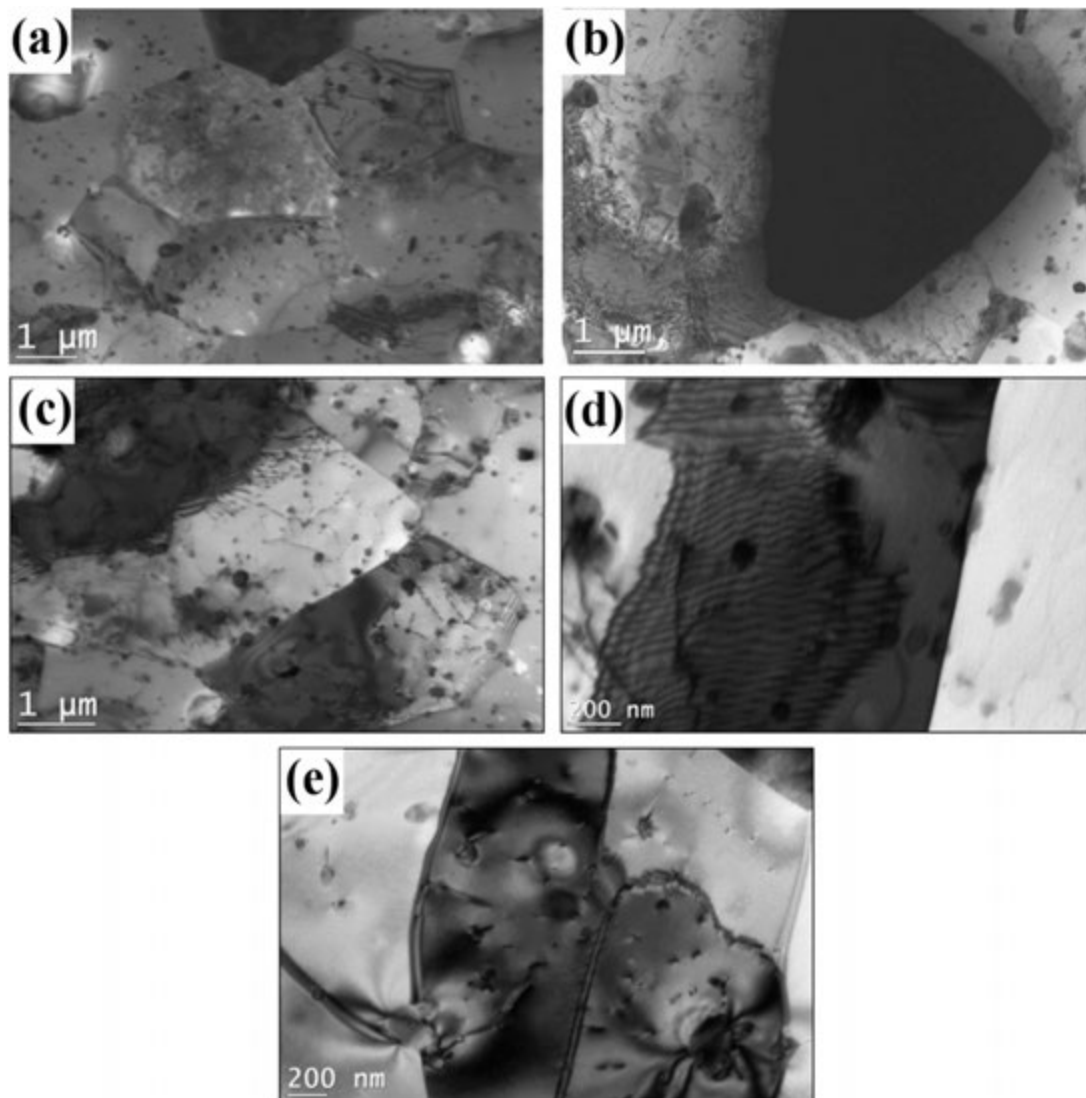


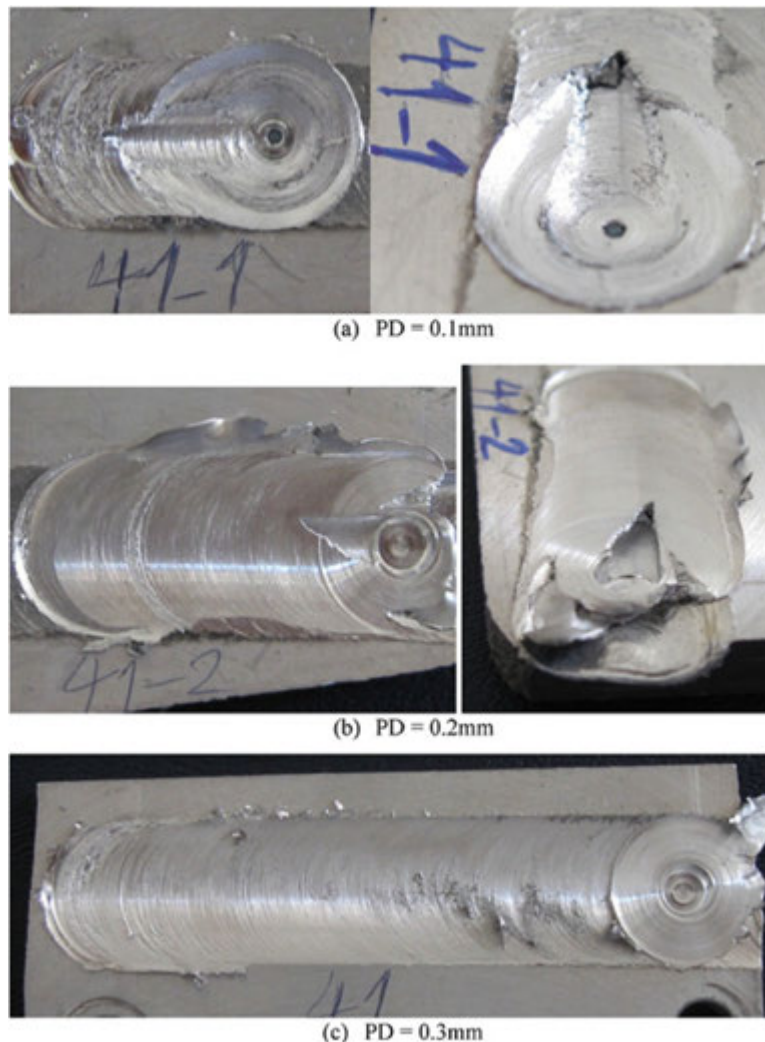
Fig. 8 TEM micrographs of 5083 Al-W composite showing: (a) fine equiaxed grains; (b) particle-matrix interface; (c) dislocation arrangement into sub-grain boundaries, (d) array of dislocations in the sub-grain boundary and (e) diffraction contrast across the sub-grain boundaries. Reproduced from Bauri, R., Yadav, D., Shyam Kumar, C.N., Balaji, B., 2015. Tungsten particle reinforced Al5083 composite with high strength and ductility. *Materials Science and Engineering A* 620, 67–75.

Magnesium Matrix Composites

Magnesium is the lightest material which is in demand in automotive industries to improve fuel economy by reducing the weight of the structures. Therefore, magnesium composites are wanted to replace aluminum alloys and its composites in some applications. FSP is a suitable method to produce such composites because it is so difficult to fabricate magnesium composites by liquid metallurgy routes (Ratna Sunil *et al.*, 2016). An overview of various magnesium composites by FSP technique is presented in **Table 2**. Several kind of reinforcement particles including SiC (Naser and Darras, 2017; Sun *et al.*, 2012), Al_2O_3 (Faraji *et al.*, 2011; Faraji and Asadi, 2011), TiC (Balakrishnan *et al.*, 2015), SiO_2 (Lee *et al.*, 2006; Khayyamin *et al.*, 2013), ZrO_2 (Navazania and Dehghani, 2016), CNT (Lu *et al.*, 2013), fly ash (Dinakaran *et al.*, 2019), C_{60} molecule (Morisada *et al.*, 2006), hydroxyapatite (Ratna Sunil *et al.*, 2014), and carbon fibers (Mertens *et al.*, 2015) were successfully used to produce magnesium composites. Magnesium has hexagonal closed packed structure and a brittle material. It is difficult to plasticize unlike aluminum. Therefore, the processing window to obtain successful composite is narrow. **Fig. 9** shows typical defects occurring on the crown during the fabrication of AZ31/SiC MMC reported by Asadi *et al.* (2010) The microstructural features are similar to the features observed in aluminum composites. Appropriate choice of process parameters would provide a uniform distribution of reinforcement particles across the stir zone with strong interfacial bonding (**Fig. 9**).

Table 2 Magnesium matrix composites fabricated by friction stir processing

Matrix	Reinforcement	Size	Reference
AZ31B	SiC	250 μm	(Naser and Darras, 2017)
AZ63	SiC	40 nm	(Sun <i>et al.</i> , 2012)
AZ91	Al_2O_3	3 μm , 0.3 μm and 30 nm	(Faraji <i>et al.</i> , 2011)
AZ31	TiC	4 μm	(Balakrishnan <i>et al.</i> , 2015)
AZ91	SiO_2	10 nm	(Khayyamin <i>et al.</i> , 2013)
AZ31	ZrO_2	40 nm	(Navazania and Dehghani, 2016)
AZ31	CNT	30 nm	(Lu <i>et al.</i> , 2013)
AZ31	Fly ash	10 μm	(Dinakaran <i>et al.</i> , 2019)
AZ31	C_{60}	100 nm	(Morisada <i>et al.</i> , 2006)
Mg	Hydroxyapatite	20 nm	(Ratna Sunil <i>et al.</i> , 2014)
AZ31B	Carbon fiber	15–30 μm	(Mertens <i>et al.</i> , 2015)

**Fig. 9** Effect of penetration depth (PD) on surface quality and defects in AZ31/SiC MMCs. Reproduced from Asadi, P., Faraji, G., Besharati, M.K., 2010. Producing of AZ91/SiC composite by friction stir processing (FSP). *International Journal of Advanced Manufacturing Technology* 51, 247–260.

Copper Matrix Composites

Pure copper is used in many industries because of its high thermal and electrical conductivity, plasticity, softness, and formability. However, poor wear resistance, low hardness, and strength limit its applications and service life in components subjects to tensile loads and sliding wear. Pure copper connectors undergo premature wear in electrical breakers. Therefore, various particles are

Table 3 Copper matrix composites fabricated by friction stir processing

Matrix	Reinforcement	Size	Reference
Cu	SiC	25 μm	(Akramifard <i>et al.</i> , 2014)
Cu	Al_2O_3	20 μm	(Suvama Raju and Kumar, 2014)
Cu	TiO_2	40 nm	(Heidarpour <i>et al.</i> , 2019)
Cu	Y_2O_3	3.5 μm	(Avettand-Fènoël <i>et al.</i> , 2014)
Cu	TiC	25 μm	(Sabbaghian <i>et al.</i> , 2014)
Cu	B_4C	4 μm	(Sathiskumar <i>et al.</i> , 2013)
Cu	WC	5 μm	(Khosravi <i>et al.</i> , 2014)
Cu	TiB_2	6 μm	(Dinaharan <i>et al.</i> , 2017c)
Cu	AlN	1 μm	(Saravanakumar <i>et al.</i> , 2017)
Cu	Fly ash	8.2 μm	(Kumar <i>et al.</i> , 2018a)
Cu	Rice husk ash	5 μm	(Dinaharan <i>et al.</i> , 2017a)
Cu	Zircon sand	96 μm	(Kumar <i>et al.</i> , 2018b)
Cu	CNT	20–30 nm	(Jafari <i>et al.</i> , 2015)
Cu	Graphite	5 μm	(Sarmadi <i>et al.</i> , 2013)
Cu	BN	1 μm	(Thankachan <i>et al.</i> , 2018)
Cu	Polymer SiCN	10 μm	(Kumar <i>et al.</i> , 2015)
Cu–Ni	ZrC	5 μm	(Priyadharshini <i>et al.</i> , 2017)
Cu–Al–Ni–Fe	BaTiO_3	–	(Thapliyal and Dwivedi, 2018)
Cu–Al–Ni–Fe	Graphite	–	(Thapliyal and Dwivedi, 2016)

reinforced to produce copper composite. FSP is a good choice to produce copper composites compared to other liquid processing methods (Ebrahimi and Par, 2019). An overview of various copper composites by FSP technique is presented in Table 3. Several kind of reinforcement particles including SiC (Akramifard *et al.*, 2014), Al_2O_3 (Suvama Raju and Kumar, 2014), TiO_2 (Heidarpour *et al.*, 2019), Y_2O_3 (Avettand-Fènoël *et al.*, 2014), TiC (Sabbaghian *et al.*, 2014), B_4C (Sathiskumar *et al.*, 2013), WC (Khosravi *et al.*, 2014), TiB_2 (Dinaharan *et al.*, 2017c), AlN (Saravanakumar *et al.*, 2017), fly ash (Kumar *et al.*, 2018a), rice husk ash (Dinaharan *et al.*, 2017a), zircon sand (Kumar *et al.*, 2018b), CNT (Jafari *et al.*, 2015), graphite (Sarmadi *et al.*, 2013), BN (Thankachan *et al.*, 2018), Polymer derived SiCN (Kumar *et al.*, 2015), ZrC (Priyadharshini *et al.*, 2017), and BaTiO_3 (Thapliyal and Dwivedi, 2018) were successfully used to produce copper composites. Pure copper (Akramifard *et al.*, 2014; Suvama Raju and Kumar, 2014; Heidarpour *et al.*, 2019; Avettand-Fènoël *et al.*, 2014; Sabbaghian *et al.*, 2014; Sathiskumar *et al.*, 2013; Khosravi *et al.*, 2014; Dinaharan *et al.*, 2017c; Saravanakumar *et al.*, 2017; Kumar *et al.*, 2018a; Dinaharan *et al.*, 2017a; Kumar *et al.*, 2018b; Jafari *et al.*, 2015; Sarmadi *et al.*, 2013; Thankachan *et al.*, 2018; Kumar *et al.*, 2015) and its alloys such as Cu–Ni (Priyadharshini *et al.*, 2017) and Cu–Al–Ni–Fe (Thapliyal and Dwivedi, 2018; Thapliyal and Dwivedi, 2016) were used as matrix material. Since copper has high melting point, the FSP tool should possess high hot hardness for successful processing. Many microstructural features are similar to aluminum and magnesium composite.

Fig. 10 shows micrographs of Cu/ TiB_2 MMCs fabricated by Dinaharan *et al.* (2017c). The micrographs show the distribution of TiB_2 particles at various volume fraction. The nature of distribution and reinforcement are seen in those micrographs. The distribution of particles covers the total area of the micrographs. Particles are separated by various distances known as interparticle distance. Therefore, the distribution of TiB_2 particles in the copper matrix can be considered as nearly homogenous. The mechanical action of the tool is accountable for the distribution of particles into the plasticized copper. The predominant process parameters of FSP process are tool rotational speed and traverse speed. Both the parameters exert an influence on the distribution of particles. The interparticle distance increases with an increase in tool rotational speed and decrease with traverse speed. Barmouz *et al.* (2011) observed good dispersion of reinforcement particles at lower traverse speed and aggregation of particles at higher traverse speed. So, a better distribution of TiB_2 particles can be ascribed to optimum conditions prevailing under the enforced experimental parameters. There was adequate time for the plasticized copper layers to go around the tool several times to be reinforced with TiB_2 particles before consolidation. There is also no chain of TiB_2 particles in the micrographs. Such an arrangement commonly forms in casting methods along the grain boundaries which is known as segregation (Ebrahimi and Par, 2019). The velocity of the solidification front and the solidification pattern often result in segregation. There is no solidification in FSP which does not result in particle movement once the plasticized composite is consolidated at the back of the tool. The particles within the forged composite will not move freely during the process of cooling to the ambient temperature. Absence of segregation indicates that the distribution of TiB_2 particles is not intergranular. Nevertheless, many TiB_2 particles may be located on the grain boundaries. Although, intragranular distribution, i.e., particles enclosed within a grain is preferred to obtain higher properties, the difference in the size of TiB_2 particles and grain size decides the nature of distribution.

Fig. 11 represents a montage of the TEM micrographs of Cu/18 vol% rice husk ash MMC prepared by Dinaharan *et al.* (2017a). The micrographs (Fig. 11(a) and (b)) are covered with ultrafine grains as well as high dislocation density. Inner regions of some grains are plain which indicates that the dislocation density is lower. The reason can be related to discontinuous dynamic recrystallization. The following factors contribute to the generation of dislocation density in the composite. Primarily, copper is subjected to severe plastic deformation throughout the FSP process. A deformed material automatically gives birth to dislocations.

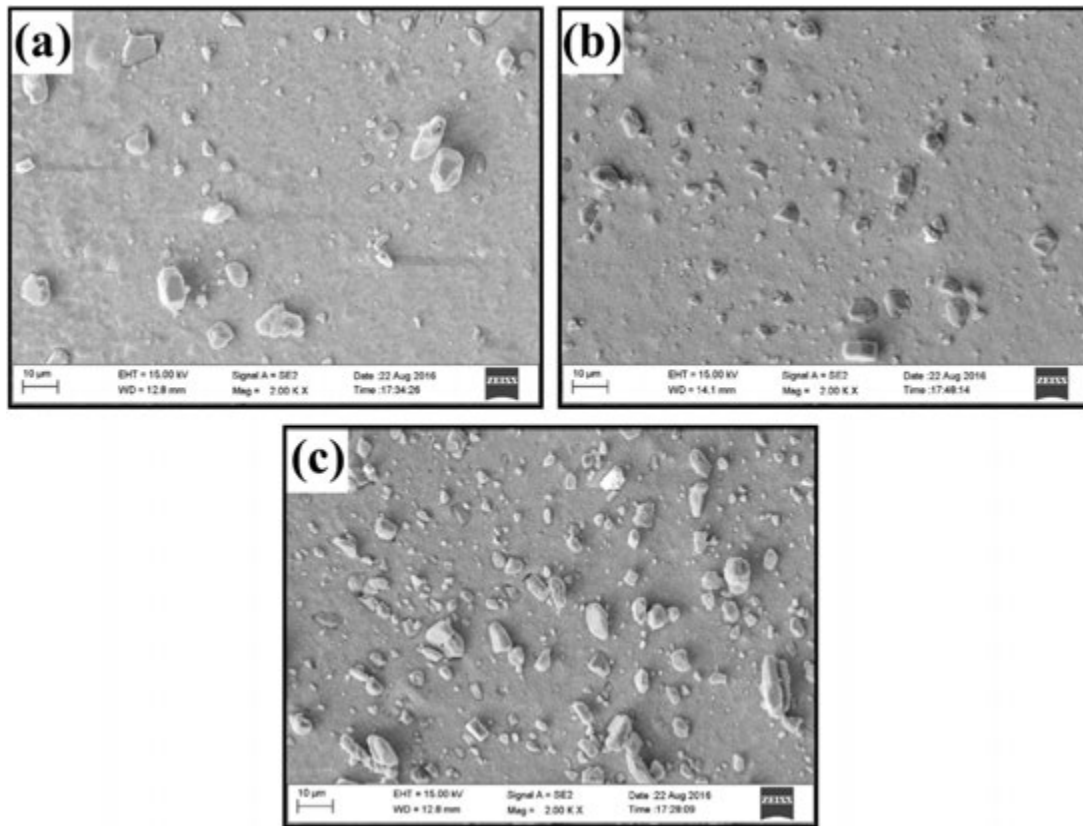


Fig. 10 FESEM micrographs of Cu/TiB₂ MMCs containing TiB₂: (a) 6 vol%, (b) 12 vol%, and (c) 18 vol%. Reproduced from Dinaharan, I., Saravanakumar, S., Kalaiselvan, K., Gopalakrishnan, S., 2017c. Microstructure and sliding wear characterization of Cu/TiB₂ copper matrix composites fabricated via friction stir processing. *Journal of Asian Ceramic Societies* 5, 295–303.

The grains in the stir zone experience a cycle of recrystallization and deformation before forging at the back of the tool. Further, the coefficient of thermal expansion of copper and rice husk ash particles are different. This variation creates an extra amount of dislocations. Entangled dislocations and pinned grain boundaries are shown in Fig. 11(c). There are numerous rice husk ash particles in the composite which are below micro level in size. Those particles improve the Zener-pinning effect which results in the formation of ultra-fine grains. Annealing twins are noticed in the composite (Fig. 11(d)). Conventionally etched and optical micrographs do not present a clear view of twins in the stir zone. Dynamically recrystallized grains of copper go through annealing process during FSP (Xue *et al.*, 2010). A growth fault may be initiated at the interaction points of several grain boundaries. This growth fault turns to be a twin. The fine grains in the composite confirm that the annealing effect is not well pronounced to coarsen the grains. The interface between a rice husk ash particle and copper matrix is seen in Fig. 11(e). There is no reaction layer around the particle.

Steel Matrix Composites

Steel is used widely as a structural material in industry and construction. However, the wear resistance of steel is considered to be poor in certain applications. Dispersion of hard ceramic particles in the steel matrix can improve strength and wear resistance compared to those of the monolithic counterparts (Ram Prabhu *et al.*, 2014; Mahathanabodee *et al.*, 2013). Conventionally, power metallurgy route is used to make steel composites which is not economical. FSP is an attractive method to produce steel-based composites. An overview of various steel composites by FSP technique is presented in Table 4. Several kind of reinforcement particles including Al₂O₃ (Kahrizangi *et al.*, 2015), TiC (Kahrizangi and Bozorg, 2012), B₄C (Joshi *et al.*, 2017), and TiB₂ (Newishy *et al.*, 2013) were successfully used to produce steel composites. Mild steel is the only material used for making the composites. The high melting point and high strength of steel imposes severe challenge on the tool. The tool undergoes enormous wear within few meters of processing. WC (Kahrizangi *et al.*, 2015; Kahrizangi and Bozorg, 2012; Joshi *et al.*, 2017) and WC–C (Newishy *et al.*, 2013) based tools were used for processing. Therefore, limited works were carried out on steel composites by FSP. Some of the microstructural features are presented in Figs. 12 and 13. Kahrizangi *et al.* (2015) observed that the preplaced Al₂O₃ nanoparticles were found to be non-uniformly dispersed in the stir zone (Fig. 12(a)) after the first FSP pass. A subsequent FSP pass (second pass) resulted in improved dispersion of the clustered Al₂O₃ particles which is attributed to the stirring action of FSP. A limited number of regions associated with the clustered Al₂O₃ particles was discerned (Fig. 2(b)) after the fourth FSP pass. Higher magnification SEM

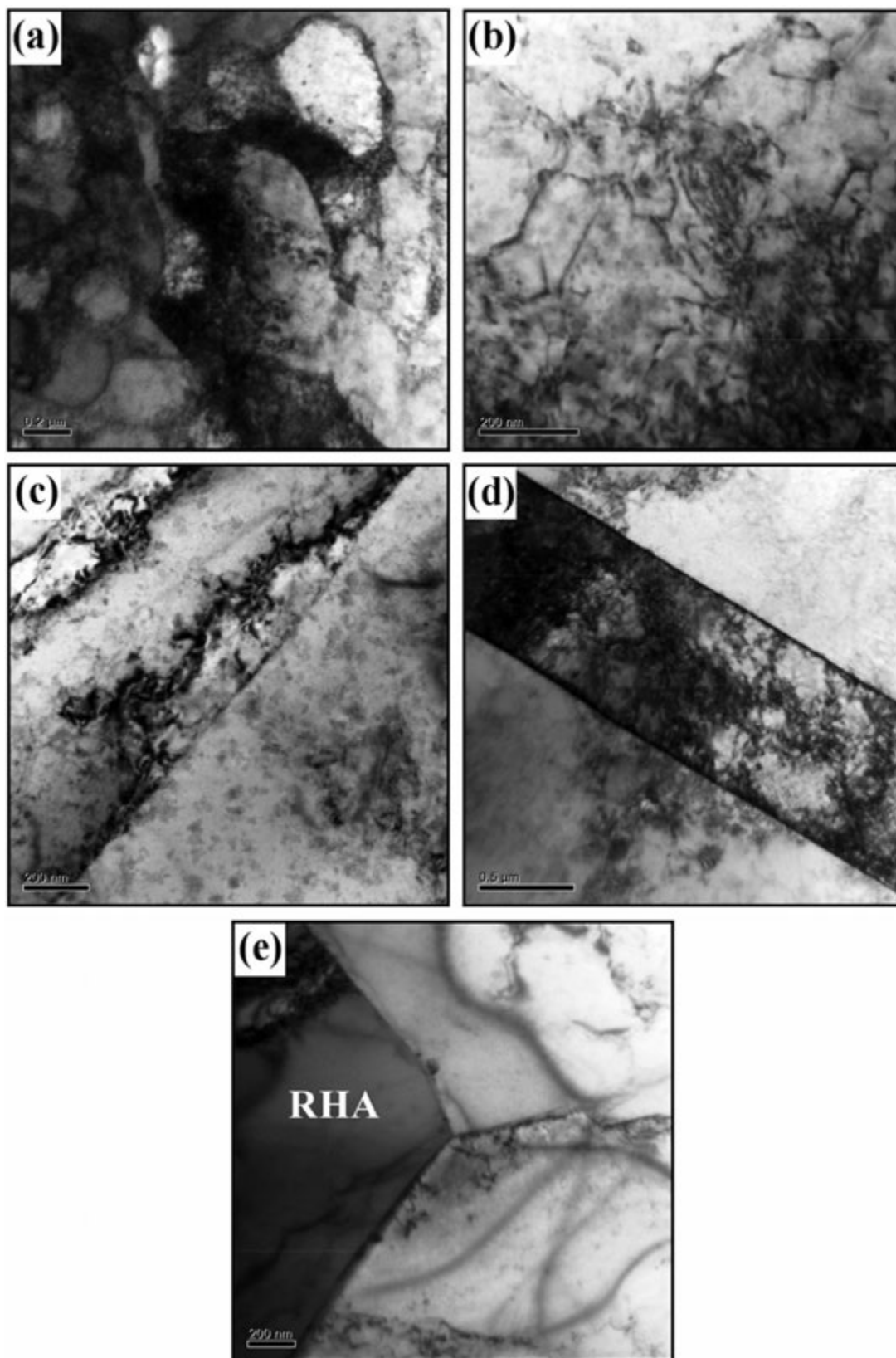


Fig. 11 TEM micrographs of Cu/18 vol% rice husk ash MMCs showing: (a) ultra-fine grains, (b) dislocation density, (c) pinning of dislocations, (d) annealing twins, and (e) interface. Reproduced from Dinaharan, I., Kalaiselvan, K., Akinlabi, E.T., Paulo Davim, J., 2017a. Microstructure and wear characterization of rice husk ash reinforced copper matrix composites. *Journal of Alloys and Compounds* 718, 150–160.

Table 4 Steel matrix composites fabricated by friction stir processing

Matrix	Reinforcement	Size	Reference
Mild Steel	Al ₂ O ₃	70 nm	(Kahrizsangi <i>et al.</i> , 2015)
Mild Steel	TiC	70 nm	(Kahrizsangi and Bozorg, 2012)
Mild Steel	B ₄ C	–	(Joshi <i>et al.</i> , 2017)
Mild Steel	TiB ₂	2 μm	(Newishy <i>et al.</i> , 2013)

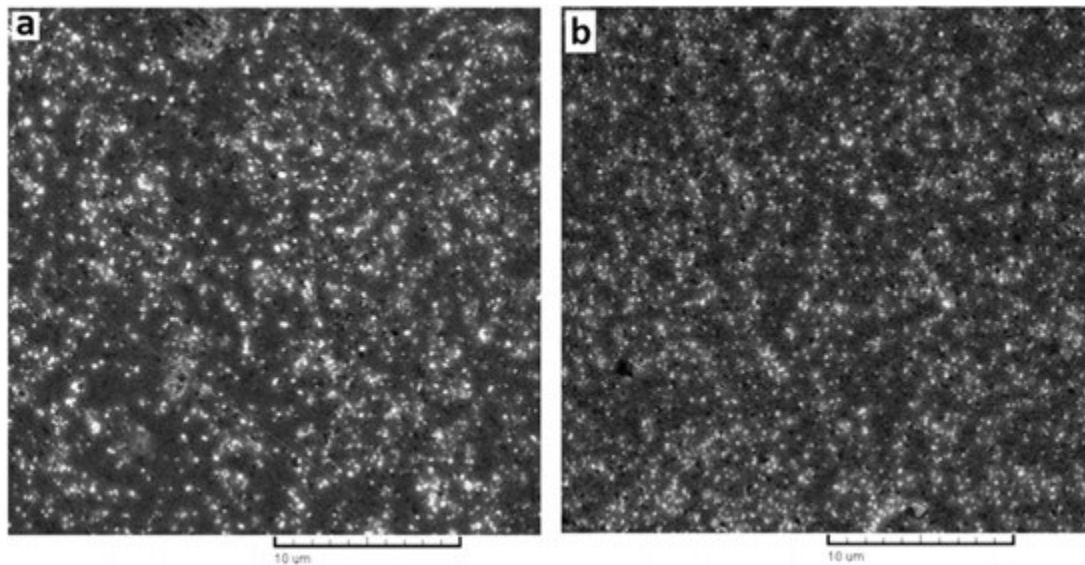


Fig. 12 SEM micrographs of mild steel composite produced using (a) one and (b) four FSP passes showing distribution of Al₂O₃ particles (with bright contrast) within the stir zone. Reproduced from Kahrizsangi, A.G., Bozorg, S.F.K., Javadi, M.M., 2015. Effect of friction stir processing on the tribological performance of steel Al₂O₃ nanocomposites. *Surface and Coatings Technology* 276, 507–515.

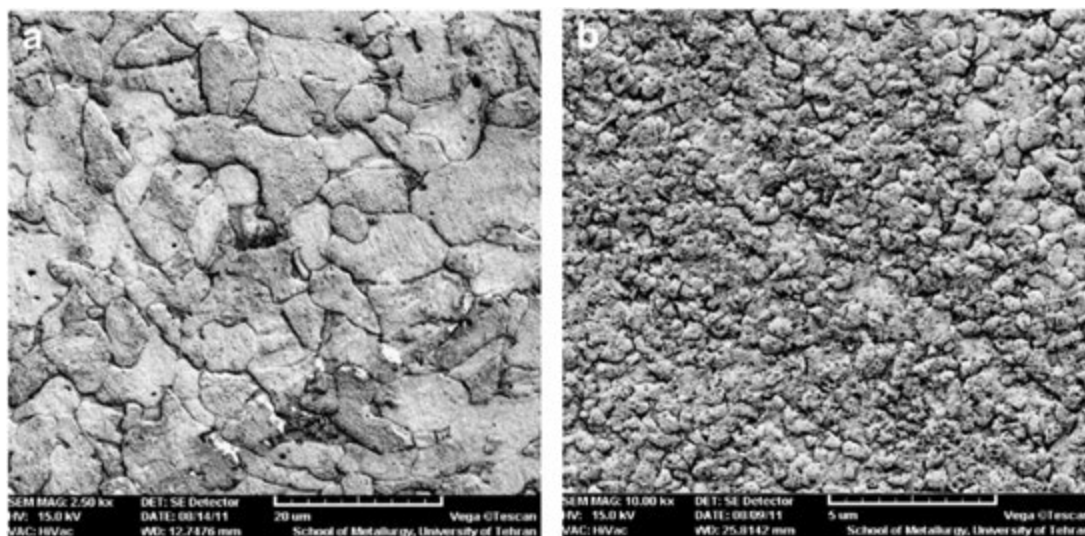


Fig. 13 The grain structure of stir zone (a) without particles and (b) after introduction of TiC particles by four FSP passes. Reproduced from Kahrizsangi, A.G., Bozorg, S.F.K., 2012. Microstructure and mechanical properties of steel/TiC nano-composite surface layer produced by friction stir processing. *Surface and Coatings Technology* 209, 15–22.

examination demonstrated the dispersion and cluster size of the Al_2O_3 particles to be a function of the number of FSP passes. Multi FSP passes produced uniform dispersion of the nano-sized Al_2O_3 particles and consequently fabricated an appropriate composite with respect to the microstructure. The grain structure evolution in the stir zone of TiC reinforced composites observed by Kahrizsangi and Bozorg (2012) is shown in Fig. 13. The stir zone showed a fine grain microstructure (Fig. 13(a)). Matrix mean grain size was measured to be $\sim 5 \mu\text{m}$ after four numbers of passes. Fine grains of the fabricated surface layer in comparison to those of the unaffected mild steel substrate, reflect the occurrence of a dynamic recrystallization process. A steel/TiC nanocomposite after four numbers of FSP passes exhibited a mean grain size of $\sim 600 \text{ nm}$ (Fig. 13(b)). Nano-sized distribution of TiC reinforcements had an extra contribution in decreasing the matrix grain size by pinning effect which retarded the grain growth process.

Titanium Matrix Composites

Titanium and its alloys are used in aerospace, petroleum, automobile, defense, and biomedical industries due to several covetable properties including superior corrosion resistance. However, they suffer high friction coefficient, poor wear resistance and loss in mechanical strength at high temperatures. Reinforcing with various particles to produce titanium composites will improve the sliding wear and friction characteristics (Tjong and Mai, 2008; Morsi and Patel, 2007). Several methods such as powder metallurgy, spark plasma sintering, vacuum arc remelting, reactive hot pressing, laser metal deposition, and induction skull melting are used for making titanium composites. Recently, FSP has been applied to produce titanium composites. An overview of various titanium composites by FSP technique is presented in Table 5. Several kinds of reinforcement particles including SiC (Shamsipur *et al.*, 2011), Al_2O_3 (Zarghani *et al.*, 2015), TiO_2 (Zhang *et al.*, 2017), TiC (Li *et al.*, 2013), TiB_2 (Wang *et al.*, 2019a), TiN (Shamsipur *et al.*, 2013), Ag (Wang *et al.*, 2019b), and hydroxyapatite (Rahmati and Khodabakhshi, 2018) were successfully used to produce titanium composites. The challenges are similar to steel composite due to the high melting point of titanium and its alloys. WC tool was predominantly used for processing.

Some of the microstructural features are shown in Figs. 14 and 15. Shamsipur *et al.* (2011) observed that a gradual break-up of SiC clusters by increasing the number of FSP passes as presented in Fig. 14 in SiC reinforced titanium composites. Material flow is complex in FSP. Three types of motion are active in the stir zone. These are circumventing motion of surface material around the tool shoulder, torsional motion due to rotational motion of surface material within the interaction layer under the tool shoulder, and vortex motion associated with the flow of thickness material due to the action of the tool pin. Such material motions are responsible for the break-up of SiC clusters and their dispersion in CP-Ti matrix. A uniform dispersion of nano-sized SiC particles was achieved after the fourth FSP passes (Fig. 14(c)). Fig. 15 shows the microstructures observed by Wang *et al.* (2019b) in Ti-6Al-4V/Ag composites. Ag occupies most regions of the stir zone as seen from the morphologies in Fig. 15(b) and (c). The distribution of Ag streamline strips is attributed to the spinning of FSP tool. Ag agglomeration is elongated along the spin direction and is inevitably formed by the likely reason of overloaded Ag nanoparticles, while the formation of well-distributed Ag particles is attributed to the inherent merits of dispersing introduced particles by FSP. The microstructure in SZ is composed of small grains with an average grain size of $10 \mu\text{m}$ (Fig. 15(c)). Smaller grains around $5 \mu\text{m}$ are also observed as streamline strips. The rotation speed plays an important role in the heat input which can accelerate the recrystallization process. Many other factors, such as the peak temperature, strain rate, cooling rate, and tool design can also affect the average grain size directly. Small grains of around $5 \mu\text{m}$ are attributed to the Ag agglomeration, which can accelerate recrystallization there by preventing grain coarsening, as indicated in Fig. 15(c). The pile-up and tangle of dislocations are easy to form around the nano particle size of Ag. The dislocation is deposited at the original grain boundary, which can increase the storage energy of deformation and provide the shape energy for dynamic recrystallization. The introduction of Ag agglomeration can increase the dislocation density and the storage energy, which can accelerate the recrystallization. Shorter excursion time at stir zone effectively restrains grain growth thereby refining recrystallized grains. As seen from Fig. 15(d), narrowband-like structure is formed in TZ and the mean grain sizes in both stir zone and transition zone are much smaller than that in base metal. Fig. 15(e) indicates the microstructure of base metal with the average grain size of $40 \mu\text{m}$.

Effect of Process Parameters

Fig. 16 shows a list of factors which can be varied and affect the resultant microstructure and properties (Sathiskumar *et al.*, 2014). It is essential to understand the role of various process parameters on the distribution of reinforcement particles in the stir zone. It

Table 5 Titanium matrix composites fabricated by friction stir processing

Matrix	Reinforcement	Size	Reference
CP Ti	SiC	50 nm	(Shamsipur <i>et al.</i> , 2011)
CP Ti	Al_2O_3	20 and 80 nm	(Zarghani <i>et al.</i> , 2015)
Ti-6Al-4V	TiO_2	200 nm	(Zhang <i>et al.</i> , 2017)
Ti-6Al-4V	TiC	5.5 μm	(Li <i>et al.</i> , 2013)
Ti-6Al-4V	$\text{TiB}_2 + \text{TiC}$	50–200 nm	(Wang <i>et al.</i> , 2019a)
CP Ti	TiN	2 μm	(Shamsipur <i>et al.</i> , 2013)
Ti-6Al-4V	Ag	50 nm	(Wang <i>et al.</i> , 2019b)
CP Ti	Hydroxyapatite	6 μm	(Rahmati and Khodabakhshi, 2018)

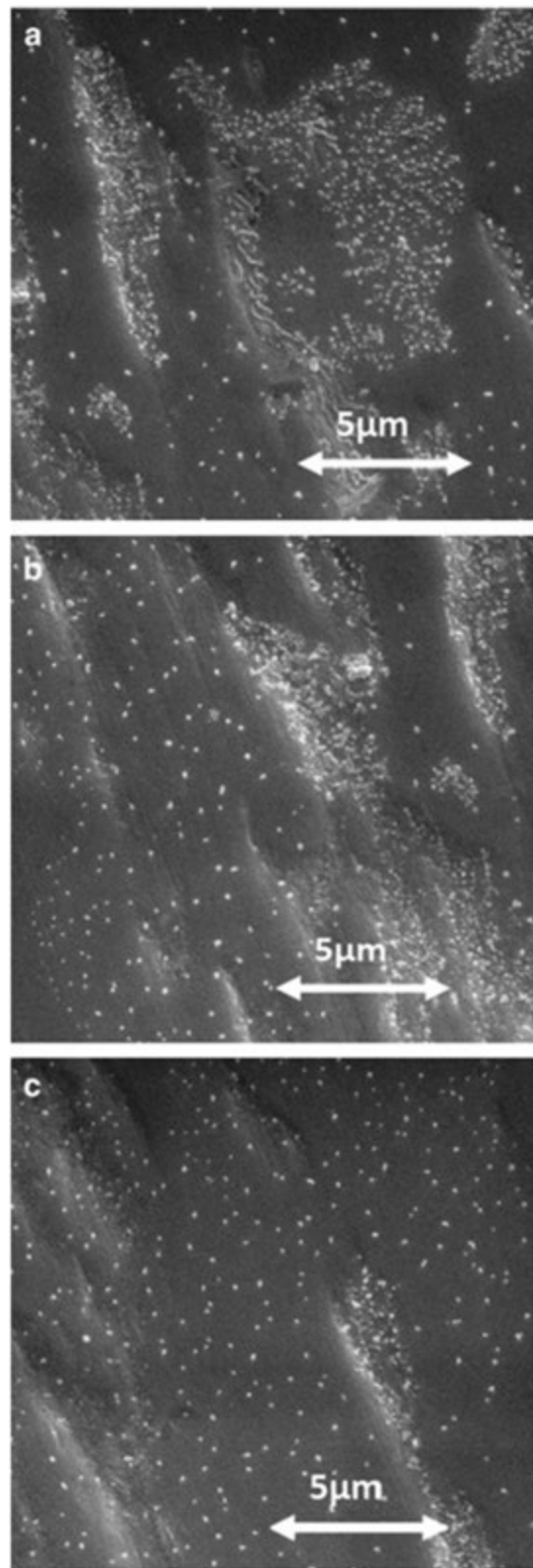


Fig. 14 SEM micrographs of SiC clusters and their dispersion in the titanium matrix as a function of FSP passes: (a) one, (b) two, and (c) four. Reproduced from Shamsipur, A., Bozorg, S.F.K., Hanzaki, A.Z., 2011. The effects of friction-stir process parameters on the fabrication of Ti/SiC nano-composite surface layer. *Surface and Coatings Technology* 206, 1372–1381.

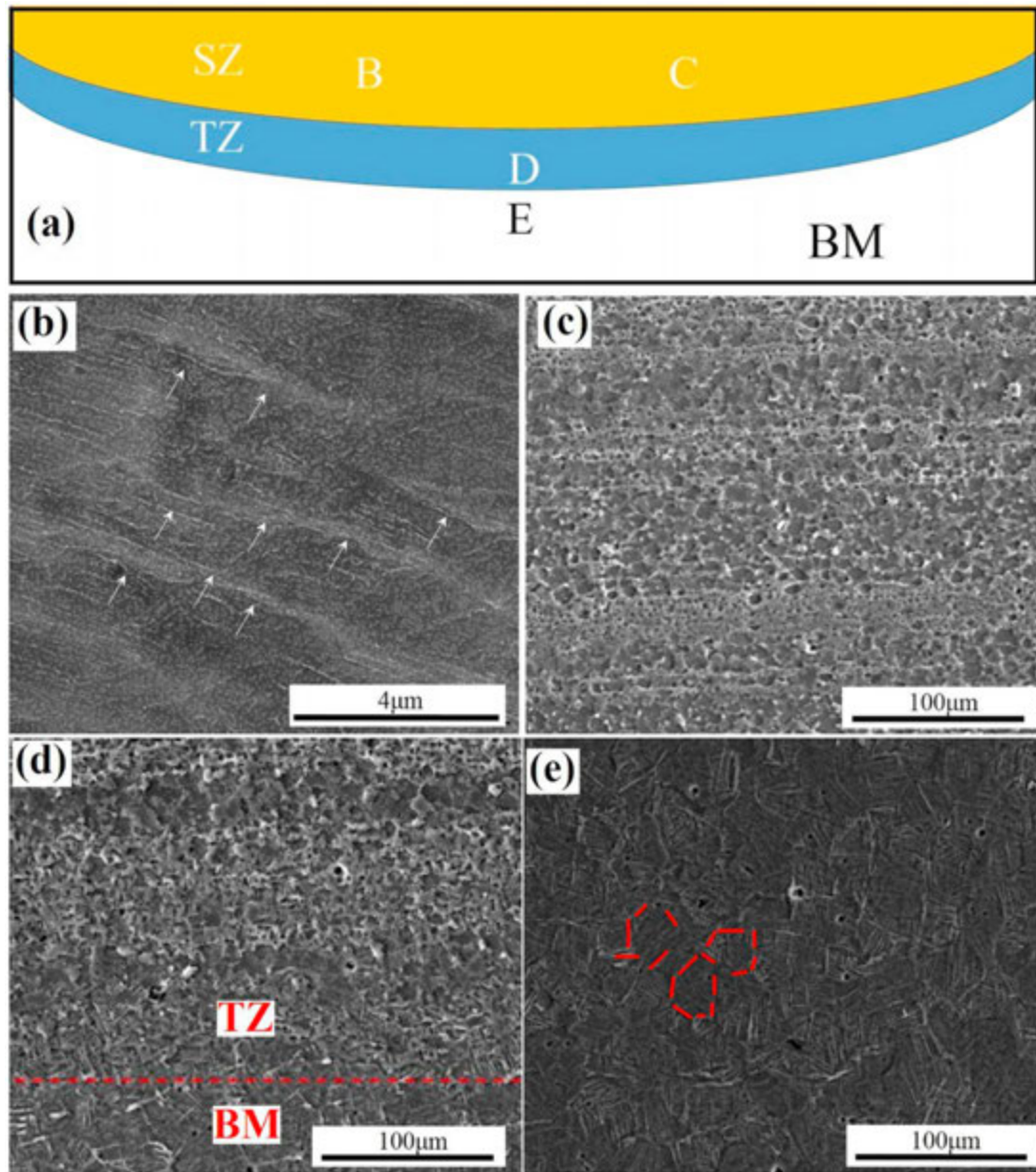


Fig. 15 SEM images of Ti-6Al-4V/Ag composites of the FSP treated specimen: (a) schematic illustration position where the SEM images were extracted; (b) and (c) are extracted from stir zone; (d) is extracted from transition zone; (e) is extracted from base metal. Reproduced from Wang, L., Xie, L., Shen, P., *et al.*, 2019b. Surface microstructure and mechanical properties of Ti-6Al-4V/Ag nanocomposite prepared by FSP. *Materials Characterization* 153, 175–183.

was found from several literature that the machine factors such as tool rotational speed, traverse speed, and number of passes influence the distribution significantly.

Tool Rotational Speed

Tool rotational speed refers to the rotating speed of the tool. The rotatory motion rubs the shoulder with the substrate plate and generate frictional heat. The rotatory motion imparts a momentum to material flow from advancing side to retreating side. The amount of frictional heat generated and the rate of material movement across the stir zone dictate the distribution of particles and grain evolution (Devaraju *et al.*, 2013; Moghaddas and Bozorg, 2013).

Fig. 17 reveals the SEM micrographs of AA6082 AMCs prepared by Dinaharan *et al.* (2016a) as a function of tool rotational speed. The influence of tool rotational speed on the distribution of TiC particles is visible. The distribution at 800 rpm (**Fig. 17(a)**) is poor. Particles are closely packed in many regions. The distribution is fairly homogenous as tool rotational speed is increased to

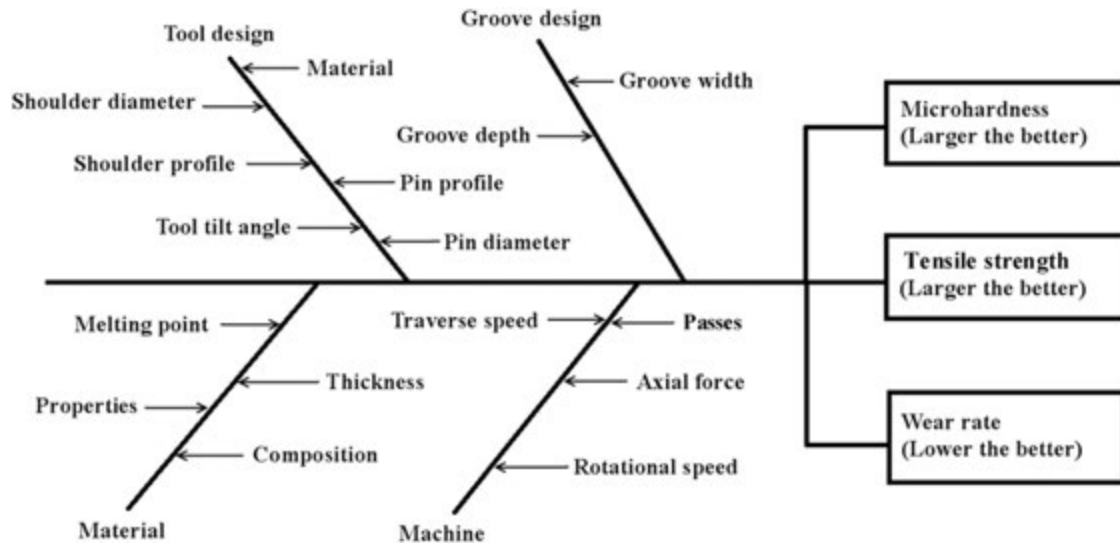


Fig. 16 FSP parameters influencing the properties of the composite. Reproduced from Sathiskumar, R., Murugan, N., Dinaharan, I., Vijay, S.J., 2014. Prediction of mechanical and wear properties of copper surface composites fabricated using friction stir processing. *Materials and Design* 55, 224–234.

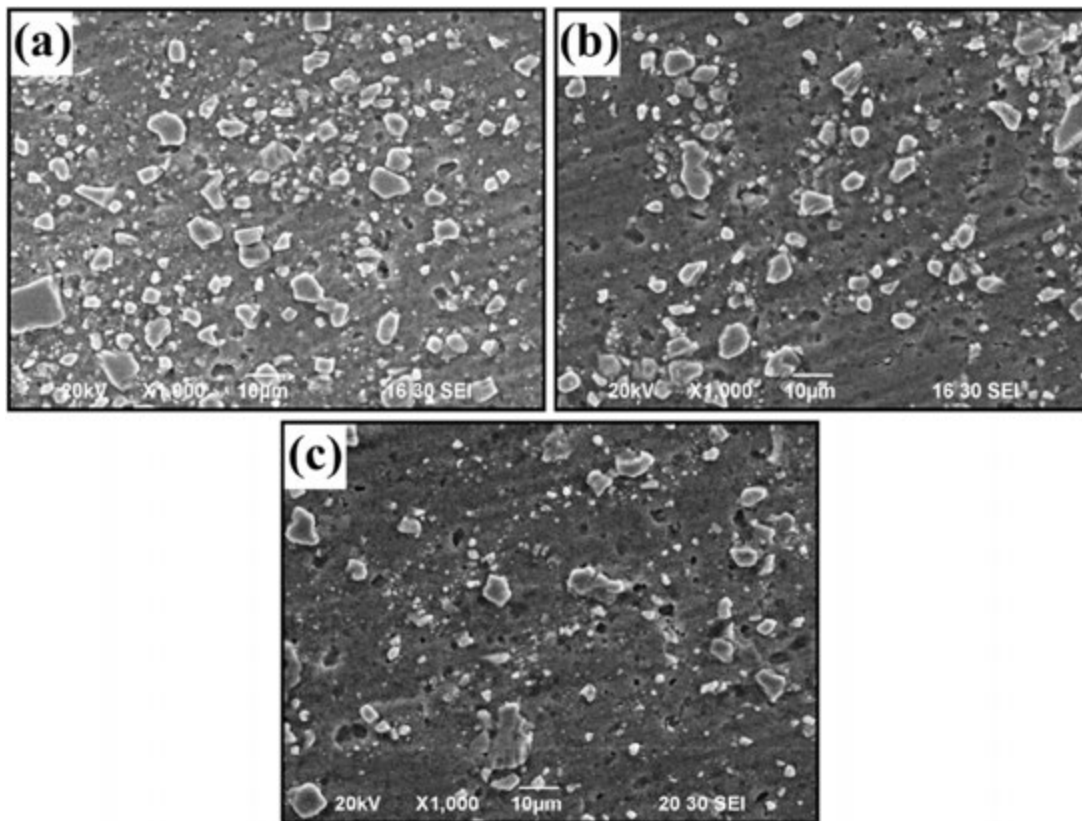


Fig. 17 SEM micrographs of AA6082 AMCs at a tool rotational speed of (a) 800 rpm, (b) 1000 rpm, and (c) 1600 rpm. Reproduced from Dinaharan, I., Murugan, N., Thangarasu, A., 2016a. Development of empirical relationships for prediction of mechanical and wear properties of AA6082 aluminum matrix composites produced using friction stir processing. *Engineering Science and Technology, an International Journal* 19, 1132–1144.

1200 rpm. The distribution further improved at 1600 rpm. The increase in tool rotational speed increased the mean interparticle distance. Apart from frictional heat generation, tool rotation stirs the plasticized material around the pin and results transportation of the plasticized material across the stir zone. The material flow from advancing side to retreating side at 800 rpm is inadequate causing poor distribution. The tool rotational speed is not sufficient enough to disperse the packed particles into all regions within

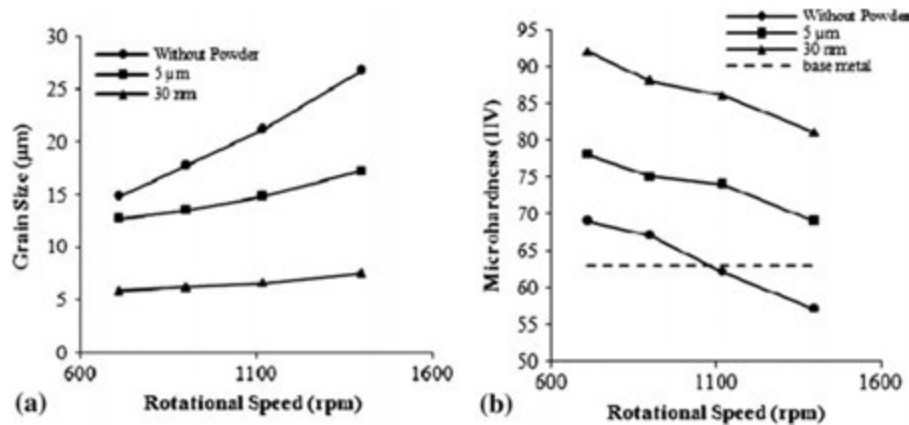


Fig. 18 Effect of the rotational speed on: (a) grain size of SZ and (b) microhardness of SZ of AZ91/SiC MMC. Reproduced from Asadi, P., Besharati Givi, M.K., Abrinia, K., Taherishargh, M., Salekroostam, R., 2011. Effects of SiC particle size and process parameters on the microstructure and hardness of AZ91/SiC composite layer fabricated by FSP. *Journal of Materials Engineering and Performance* 20, 1554–1562.

the plasticized aluminum. FSP process induces plastic strain on the processed aluminum. This plastic strain increases as tool rotation speed is increased. The enhanced plastic strain aids to disperse the particles further into the particle free regions. The agglomeration of particles fades away.

Fig. 18 shows the effects of the rotational speed on grain size and hardness of AZ91/SiC MMC with the additions of various SiC particles (Asadi *et al.*, 2011). It can be inferred from Fig. 17(a) that addition of SiC particles fades the effect of generated heat on the grain growth as the rotational speed increases. Also, the rotational speed has no significant effect on the grain size of the specimen with 30 nm SiC particles. Grains break into smaller sizes during deformation, regardless of SiC particles. Therefore, a large number of high angle grain boundaries are produced. However, in this case, addition of SiC particles leads to inhomogeneous local deformation that assists the break-up of the grains. According to Fig. 18(a), it seems that this phenomenon is highly affected by the number and size of SiC particles. While the grain size of the specimens with and without 5 μm SiC particles is rather close, there is a huge difference in the cases of specimens with nano particles. The number of 30 nm SiC particles is much more than 5 μm ones. Consequently, the effect of grain breaking is more intensive. As shown in Fig. 18(b), the higher the rotational speed, the higher the grain size, and the less the microhardness. The Hall–Petch relation expresses that the hardness has an inverse correlation with the grain size. But there is an exception. The stir zone hardness of sample without SiC particles at the rotational speed of 1400 rpm was less than that of the base metal (63 HV), despite the decrease in the grain size (from ~150 to ~27 μm). It was the result of dissolution of strengthening β ($Mg_{17}Al_{12}$) phase during the FSP.

Traverse Speed

Traverse speed determines the dwell period of the frictional heat and reduce the material movement. The effect of traverse speed on the microstructure of Cu/B₄C MMC is shown in Fig. 19. The optical micrograph of the composite fabricated at 20 mm/min shows (Fig. 19(a)) homogeneous distribution of B₄C particles. The distribution is not uniform (Fig. 19(c)) at 60 mm/min due to the poor distribution of B₄C particles at several places. When traverse speed was increased, the poor distribution of B₄C particles gradually increased. The average spacing between B₄C particles decreased when traverse speed was increased. The traverse speed governs the available stirring of rotating tool per unit length of FSP and affects the transportation of material from advancing side to retreating side. The available stirring is more at a traverse speed of 20 mm/min which results in higher plastic strain. The uniform distribution of B₄C particles as seen in the micrograph (Fig. 19(a)) can be attributed to intense stirring and sufficient material flow which reduces poor distribution. When traverse speed increases, the material flow between advancing side and retreating side becomes inadequate. Proper mixing of plasticized copper and B₄C particles does not take place which aids poor distribution.

Microhardness behavior of Cu/SiC MMCs with and without SiC particles is shown in Fig. 20 (Barmouz *et al.*, 2011). It is seen that microhardness values in the side regions of stir zone are reduced because of annealing-induced grain growth. On the one hand, stirring action of the pin leads to a dynamic recrystallization in the stir zone which reduces the grain size and enhances the dislocations which eventually improves the microhardness values. On the other hand, the annealing effect of heat input decreases the microhardness values. In the specimens processed without SiC particles at traverse speeds of 40 and 80 mm/min, despite the reduction in grain size, the annealing effect is predominant and microhardness is diminished as compared to the microhardness of the pure copper which was measured to be 70 HV. It is also to be noted that according to the results, the microhardness values in the stir zone of the aforementioned specimens are independent of grain size. Thus, other factors such as dislocation density could control the microhardness behavior. However, in the traverse speed of 200 mm/min, dynamic recrystallization dominates the annealing effect which could be due to lower heat input and higher thermomechanical stress resulting in enhancement of the microhardness values. Specimens processed with SiC particles, i.e., composites show higher microhardness values in comparison with those without SiC particles. This is due to the pinning effect and presence of hard SiC particles. Fig. 20(b) implies that higher

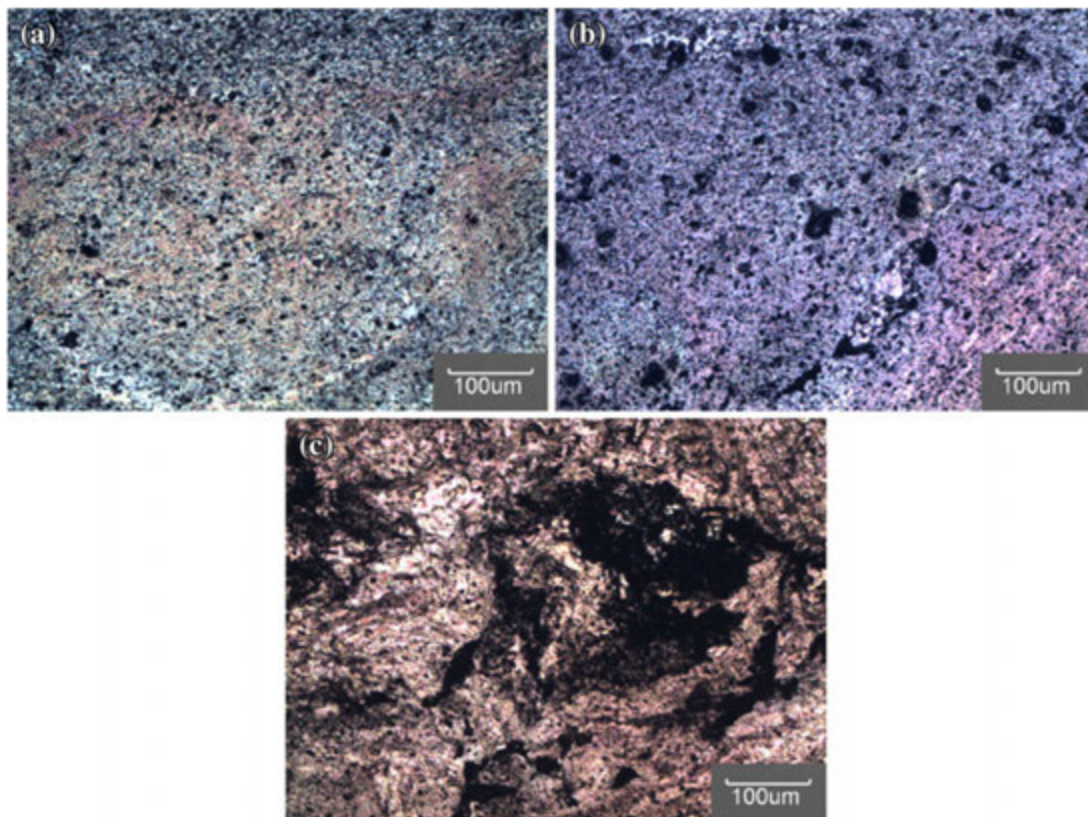


Fig. 19 Optical photomicrograph of Cu/B₄C MMC at traverse speed: (a) 20 mm/min, (b) 40 mm/min, and (c) 60 mm/min. Reproduced from Sathiskumar, R., Murugan, N., Dinaharan, I., Vijay, S.J., 2013. Effect of traverse speed on microstructure and microhardness of Cu/B₄C surface composite produced by friction stir processing. Transactions of Indian Institute of Metals 66, 333–337.

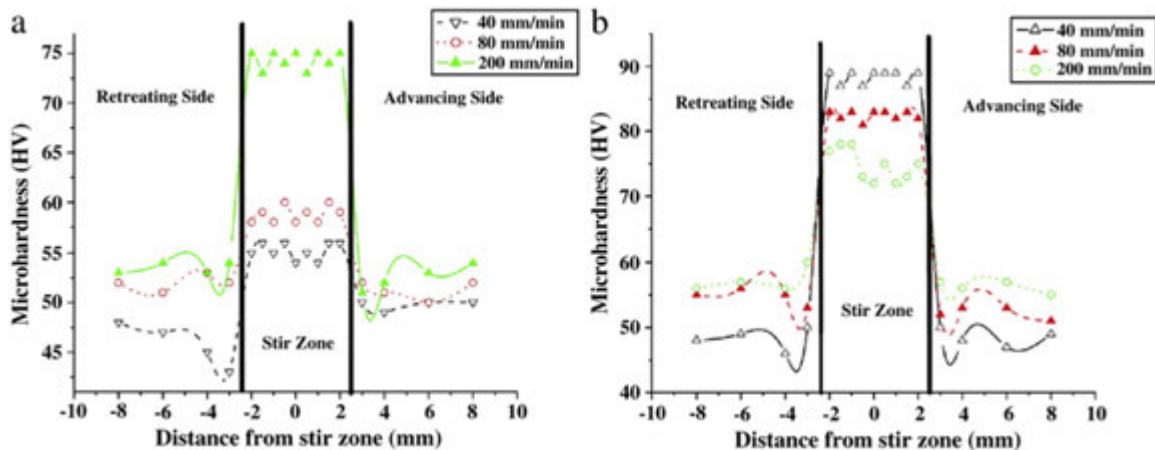


Fig. 20 Microhardness values of friction stir processed copper: (a) without SiC particles and (b) with SiC particles at different traverse speeds. Reproduced from Barmouz, M., Givi, M.K.B., Seyfi, J., 2011. On the role of processing parameters in producing Cu/SiC metal matrix composites via friction stir processing: Investigating microstructure, microhardness, wear and tensile behavior. Materials Characterization 62, 108–117.

traverse speed causes gathering of SiC particles and thus reduction of the pinning effect of SiC particles which results in lower increment of the microhardness values. Whereas for the specimens prepared at lower traverse speeds, SiC particles were separated well and consequently an intense pinning effect occurs in stir zone leading to a further enhancement of microhardness values. It was also found that due to heterogeneous distribution of SiC particles in the specimen produced at a traverse speed of 200 mm/min, the microhardness values in stir zone are not in the same range. In other words, there is a large difference between microhardness values in this zone.

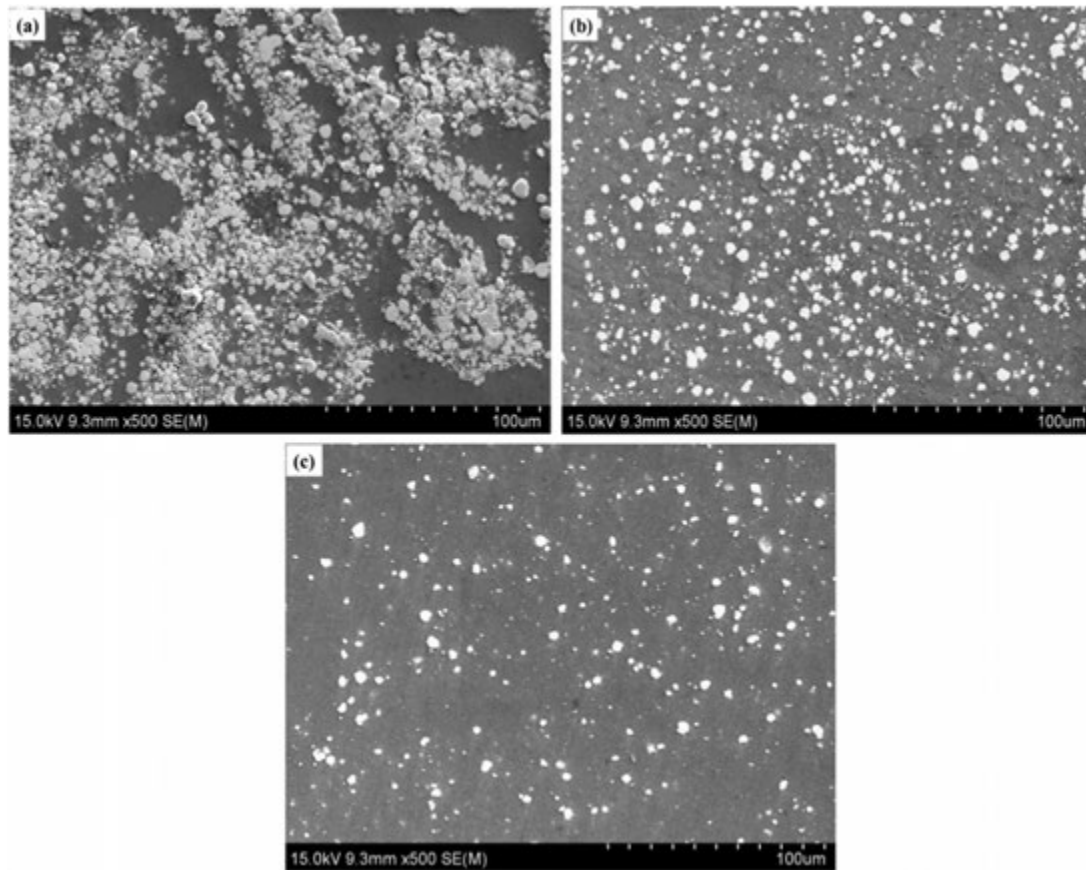


Fig. 21 SEM micrographs of AA1060/W composites after: (a) 1-pass, (b) 3-passes, and (c) 5-passes. Reproduced from Huang, G., Shen, Y., Guo, R., Guan, W., 2016. Fabrication of tungsten particles reinforced aluminum matrix composites using multi-pass friction stir processing: Evaluation of microstructural, mechanical and electrical behavior. *Materials Science and Engineering A* 674, 504–513.

Number of Passes

Passes refer to doing the same processing over the previously processed track again. It is discovered in literature that many times it is difficult to achieve proper distribution in first pass. The distribution and material flow improve with successive passes. **Fig. 21** shows the SEM micrographs of the AA1060/W composites produced by different passes (Huang *et al.*, 2016). It is clearly seen from **Fig. 21(a)** that there exist obvious W clusters and only a small amount of aluminum is immersed into W clusters in the 1-pass. This is mainly due to the following two reasons: (a) during compaction of W particles into the groove, the pressure causes the W particles to mechanically interlock and cold weld together; (b) relatively large residual strain and stress of as-received rolled aluminum plate from its manufacturing process result in insufficient material softening that leads to poor plastic flow during 1-pass FSP. As the number of FSP passes increases, the size of W clusters is significantly decreased. As shown in **Fig. 21(b)**, only a few W clusters are observed after the 3-pass. A more uniform W distribution with almost no W clusters is obtained after the 5-pass. This is attributed to more plastic deformation and thorough mixing caused by the accumulated plastic strain and the repeated thermal exposure. Nevertheless, no significant change in the size and morphology of W particles are observed as the number of FSP passes increases. This observation is at odds with the results reported by Prater (2011) who recorded that the vigorous stirring action of the tool and the intense plastic strain could break the ceramic particles and change their size and morphology. This is likely to be related to the initial smaller size of W particles. In addition, all SEM micrographs of composites show no occurrence of particle detachment during the mechanical polishing process. This may imply that an effective interface bonding is obtained. Further, this suggests the effectiveness of the 5-pass FSP process for the production of composites with uniform microstructure.

Fig. 22 also shows the stress–strain curves for the base AZ91 magnesium alloy and the specimens with nano SiO_2 powder as the reinforcement fabricated in one, two and three passes (Khayyamin *et al.*, 2013). It is expected that the as cast AZ91 magnesium alloy has the lowest UTS and elongation because of the existence of large grains ($140\text{ }\mu\text{m}$) and hard $\text{Mg}_{17}\text{Al}_{12}$ precipitates at the grain boundaries. The as-cast AZ91 magnesium alloy has a completely brittle fracture with low yield strength and UTS. It is observed in **Fig. 22** that the UTS and elongation of the composite produced in one pass increased from 139 to 193 MPa and 6.74%–12.56%, respectively, in comparison with the base metal. The main reasons of the improvement in UTS and elongation are as follows: (a) by increasing the FSP pass number, the distribution of the particles becomes more uniform;

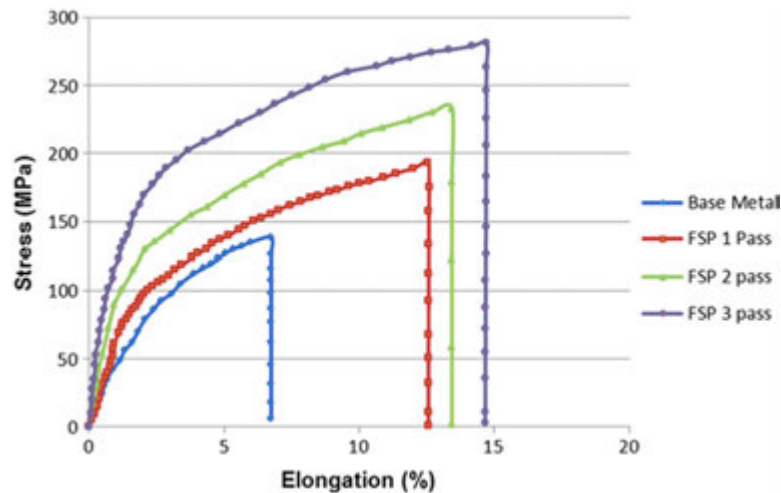


Fig. 22 Stress strain curves for base metal and AZ91/SiO₂ MMCs processed with traverse speed of 63 mm/min and rotational speed 1250 rpm in 1, 2 and 3 passes. Reproduced from Khayyamin, D., Mostafapour, A., Keshmiri, R., 2013. The effect of process parameters on microstructural characteristics of AZ91/SiO₂ composite fabricated by FSP. *Materials Science and Engineering A* 559, 217–221.

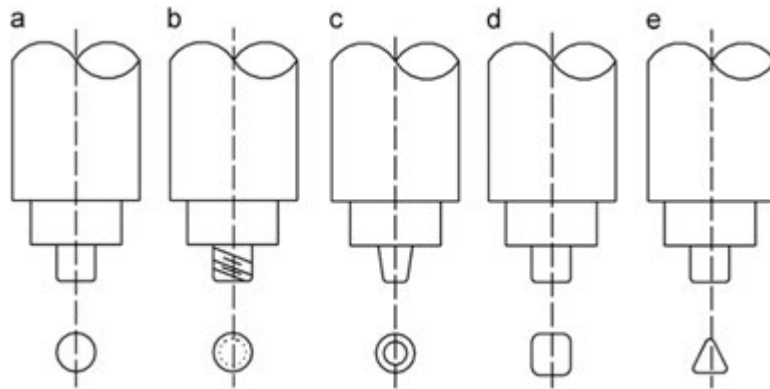


Fig. 23 FSP tool pin profile (a) Straight cylinder, (b) Threaded cylindrical, (c) Tapered Cylindrical, (d) Square, and (e) Triangle. Reproduced from Sarmadi, H., Kokabi, A.H., Reihani, S.M.S., 2013. Friction and wear performance of copper–graphite surface composites fabricated by friction stir processing. *Wear* 304, 1–12.

(b) hard precipitates of Mg₁₇Al₁₂ in the grain boundaries which are the favorable sites for starting the cracks are dissolved during processing; (c) porosities and voids of the cast alloys (**Fig. 22**).

Effect of Tool Design

Tool design refers to number of aspects including shoulder diameter, shoulder profile, pin diameter, pin profile, and tool material (Sathiskumar *et al.*, 2014; Parumandla and Adepu, 2020; Shojaeefard *et al.*, 2016; Azizieh *et al.*, 2011). All the aforementioned aspects influence the generation of frictional heat and the subsequent material flow. The particle distribution is greatly affected by the resultant material flow of the tool design. Sarmadi *et al.* (2013) used five tools with different pin profiles (straight cylindrical (SC), tapered cylindrical (TC), threaded cylindrical (TH), square (SQ), and triangular (TR)) as schematically shown in **Fig. 23** to fabricate graphite reinforced copper composites. **Fig. 24** presents optical micrographs of particles distribution using different tool pin profiles. These images were recorded from center of the stir zone. As seen in the micrographs, particles are aggregated in the center of stir zone in case of pin profiles SC, TC, and TH. Particles totally dispersed in the matrix and the distribution of particles is adequate using pin profile SQ and TR. This is related to flow patterns of copper substrate against different tools during FSP. The particle volume fraction was computed using an Image Analyzer software. It was found that the volume percent was maximum in composite produced by SC pin being 13.95%. In the case of composite produced by TR pin, the volume percent was 10.89 vol% which is the minimum value among all of the composites. Composite produced by SQ pin had 11.90 vol% graphite particles which is lower than composites produced by SC, TC, and TH pins. Lower particles volume percent of composites produced by SQ

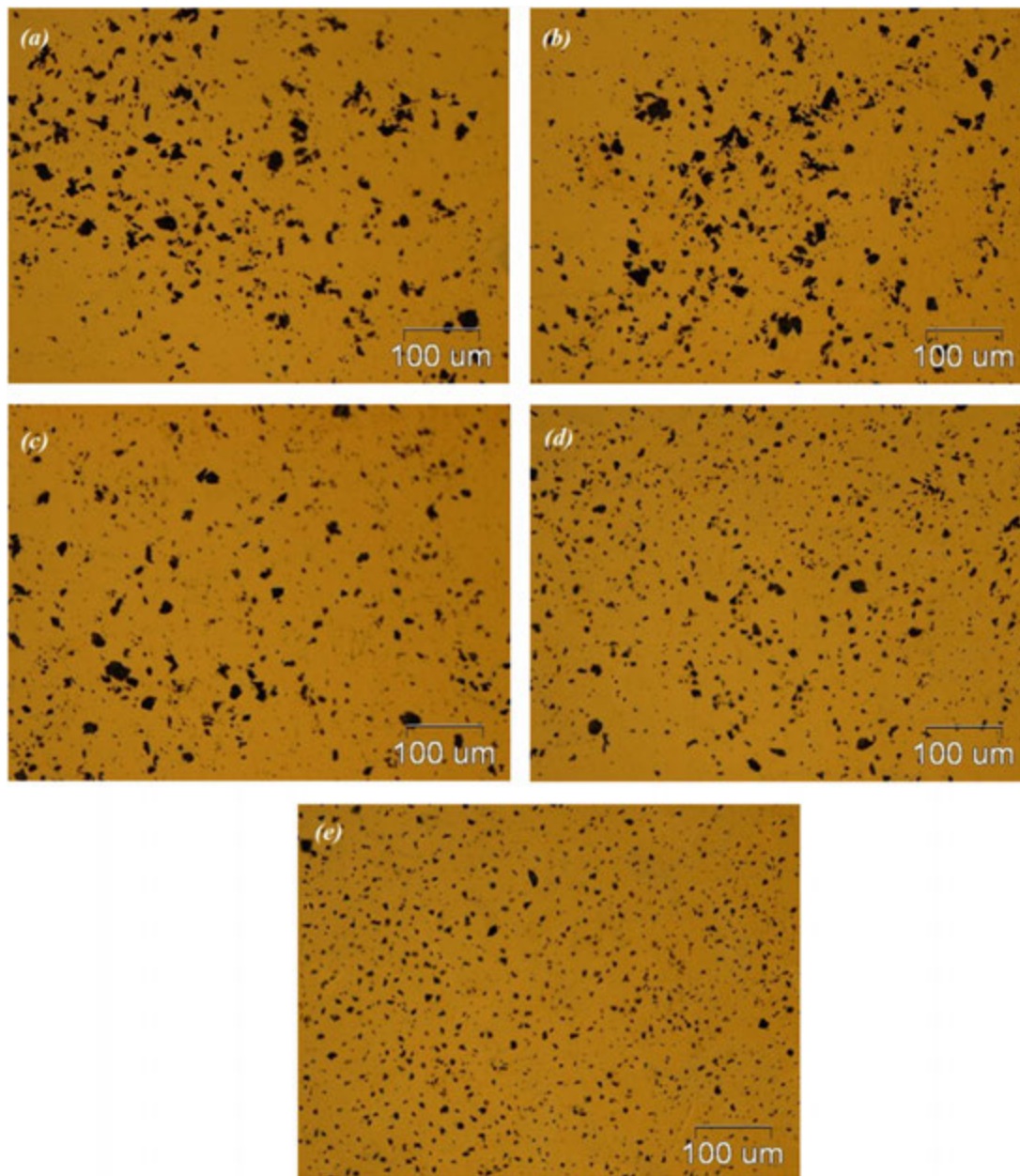


Fig. 24 Optical microscopic images from center of stir zone containing Cu/graphite composite using tool pin profile: (a) SC, (b) TH, (c) TC, (d) SQ, and (e) TR. Reproduced from Sarmadi, H., Kokabi, A.H., Reihani, S.M.S., 2013. Friction and wear performance of copper-graphite surface composites fabricated by friction stir processing. *Wear* 304, 1–12.

and TR pins showed that particles did not aggregate at the center of these composites and distribution of particles of these composites is better than three other composites. The size of largest cluster in composites using SC, TC, and TH profiles is more than 40 μm which proves that particles agglomerated and as can be seen from Fig. 24(a–c). The number of clusters were high in these composites. In the case of composites using SQ and TR profiles, the size of largest cluster is about 27 and 22 μm , respectively, which are almost the same. Consequently, better distribution of particle was reached using the tool with triangular pin.

Bahrami *et al.* (2014) employed five FSW tools with different pin geometries, i.e., threaded tapered, triangular, square, four-flute square, and four-flute cylindrical (denoted as TT, T, S, FFS, and FFC) to fabricate AA7075/SiC MMCs as presented in Fig. 25. All tools were machined out of H13 and heat treated to have 58 HRC. SEM micrographs of particle distribution in the stir zone are shown in Fig. 25. It can be inferred from these figures, that SiC particles clustered locally. Although triangular specimen showed finest cluster size, the most uniform cluster distribution was achieved in threaded tapered specimen. This can be ascribed to the improvement of material flow associated with downward motion of materials along the probe threads. On the other hand, largest clusters were observed in four-flute cylindrical specimen. This further supported the inappropriate material flow in four-flute cylindrical specimen. There was a

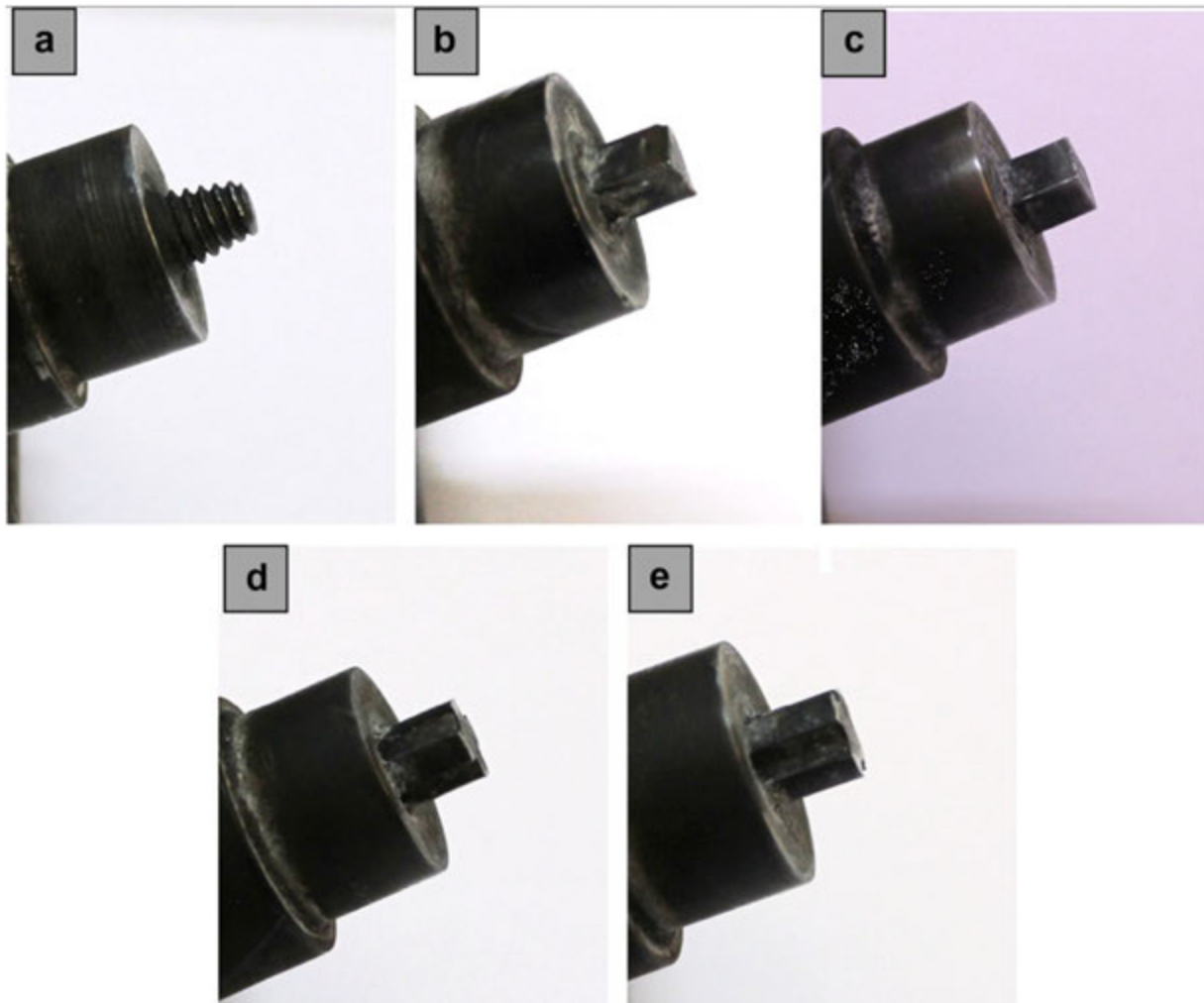


Fig. 25 Designed pin geometries: (a) threaded tapered, (b) triangular, (c) square, (d) four-flute square, and (e) four-flute cylindrical. Reproduced from Bahrami, M., Givi, M.K.B., Dehghani, K., Parvin, N., 2014. On the role of pin geometry in microstructure and mechanical properties of AA7075/SiC nano-composite fabricated by friction stir welding technique. *Materials and Design* 53, 519–527.

remarkable difference between the cluster size of four-flute cylindrical specimen and that of the other specimens. However, the remaining cluster sizes were almost identical in size. Presence of large clusters in four-flute cylindrical specimen is a good reason for lack of pulsating stirring action. Indeed, pulsating stirring action intensifies the mixing of particles in the matrix. Moreover, downward motion of materials around the pin is eliminated by the absence of threads in FFC pin. Consequently, lack of flat sides or threads are the main reasons behind severe agglomeration of the reinforcements in four-flute cylindrical specimen (Fig. 26).

Summary and Future Outlook

This article presented an overview of the FSP process to fabricate MMCs. The microstructural aspects of various metallic based MMCs were explored. The role of process parameters and tool design were also presented. FSP is an economical and energy efficient process to produce MMCs. It is possible to obtain a homogeneous distribution of reinforcement particles in the stir zone by optimizing the process parameters and tool design. FSP overcomes most of the common defects encountered in liquid metallurgy routes. A sound interface without any kind of reaction is obtained in FSP. The load bearing capacity of composites by FSP is high. The fine grains generated by dynamic recrystallization are beneficial to obtain higher properties. FSP can be used to make composites to a desirable depth either at surface level or bulk thickness by changing the tool design. Multi track grooves can be used to fabricate the composite over the entire substrate material.

There is a demand for MMCs based on high melting point alloys such as titanium, steel, and inconel. The tool design presents challenges to fabricate such composites due to the higher temperature and forces during processing. The tool design especially tool material combination should be developed for successful processing over longer processing distance. The ceramic reinforcements used for making composites interacts with the tool and caused abrasion wear. The pin geometry and profile are lost over few

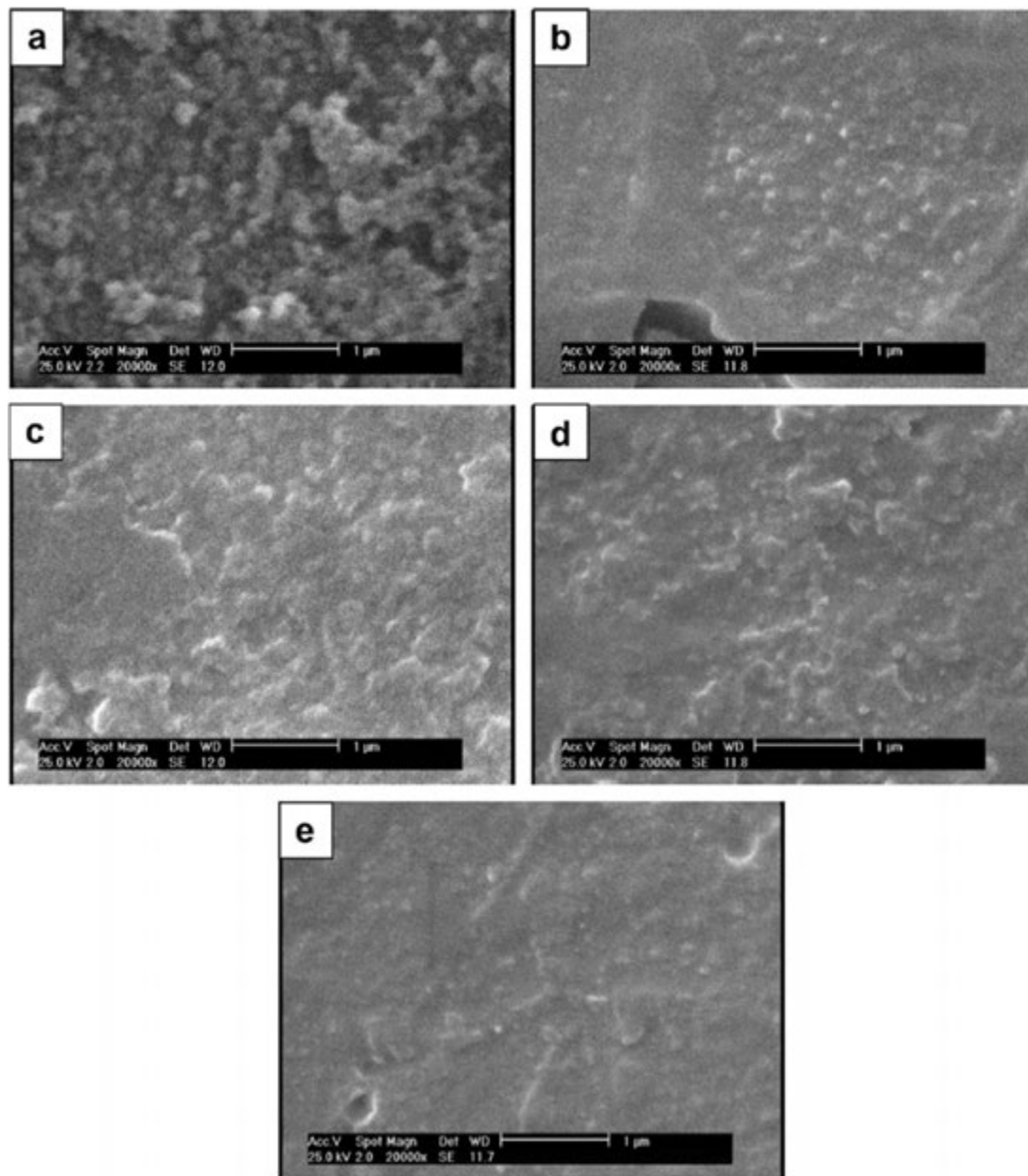


Fig. 26 Dispersion of SiC nano-particles in AA7075/SiC composites using: (a) TT, (b) T, (c) S, (d) FFS, and (e) FFC pin tool. Reproduced from Bahrami, M., Givi, M.K.B., Dehghani, K., Parvin, N., 2014. On the role of pin geometry in microstructure and mechanical properties of AA7075/SiC nano-composite fabricated by friction stir welding technique. *Materials and Design* 53, 519–527.

hundred meters of processing. There is no detailed investigation on tool wear which needs to be explored by researchers. An interest is gradually arising to use the FSP technique to produce composites based on non-metals. More research work is required to extend the process to develop polymer based composites.

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Solid State Routes for Composite Materials Production

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Introduction

Composite materials have attracted great attention in both academic and industrial domains due to their unique structure and properties. They can be divided into three main categories based on the type of their matrix phase. These categories include metals matrix composites (MMCs), polymer matrix composites (PMCs), and ceramic matrix composites (CMCs). It is worth noting that, intermetallic matrix composites (IMCs) and glass matrix composites (GMCs) are usually considered in the CMCs category. In the case of MMCs (the scope of this article), there are different production methods such as solid-state, liquid-state, and gaseous-state routes. Solid-state routes result in superior mechanical properties compared to liquid state routes due to the elimination of casting and solidification defects during the production of bulk MMCs. Furthermore, solid-state routes are usually accompanied by metallurgical phenomena such as severe plastic deformation (SPD), recrystallization, etc., which cause higher strength. In this article, we introduce different solid-state routes for the production of MMCs.

Powder Metallurgy

This manufacturing method consists of numerous production ways in which the final products are fabricated from the powder of raw materials (Cahn, 1978; Reitz, 1997) with the emphasis of producing finished and/or semi-finished products (Whittaker and Williams, 2014). The powder format of the materials used gives the advantage of the possibility to process within the controlled states of solid, liquid, and gas, which makes the Powder Metallurgy (PM) more flexible than other production techniques. Some of the process advantages noted in Fig. 1 make the PM route the only feasible solution for some production requirements (Barrow *et al.*, 1990). Between those advantages, the potential of employing hard or even otherwise un-processable materials is one of the important advantages (Anninger *et al.*, 2017; Anselmi-Tamburini and Groza, 2017). Refractory materials such as Mo, Nb, W, and Ta are some examples of those materials for which their shaping into useable components would be troublesome in the absence of powder metallurgy processing technology (Anninger *et al.*, 2017; Anselmi-Tamburini and Groza, 2017).

PM is divided into five stages: Powder Production, Mixing and Blending, Pressing, Sintering, and Finishing Operations (Anninger *et al.*, 2017; Pokorska, 2008) (see Fig. 2). A combination of these steps with specific features has led to the development of alternative PM processes. The Powder Forging (Park *et al.*, 2001; Hartley and Pillinger, 2006; Qiu *et al.*, 2012), Hot Isostatic (HIP) (Abouaf *et al.*, 1988; Bocanegra-Bernal, 2004), Metal Injection Molding (MIM) (Heaney, 2018), Electric Current Assisted Sintering (ECAS) (Anselmi-Tamburini and Groza, 2017; Lagos *et al.*, 2017; Becker *et al.*, 2018), and Powder Based Additive Manufacturing (AM) (Dawes *et al.*, 2015; Singh *et al.*, 2017; Froes *et al.*, 2019) are some of the main PM processes which have been developed (Akhtar *et al.*, 2018).

At the first step of the PM process, the powder materials should be produced. These powders based on final expectations can be altered in size and shape during the production processes. The physical and chemical nature of produced powders is also affected

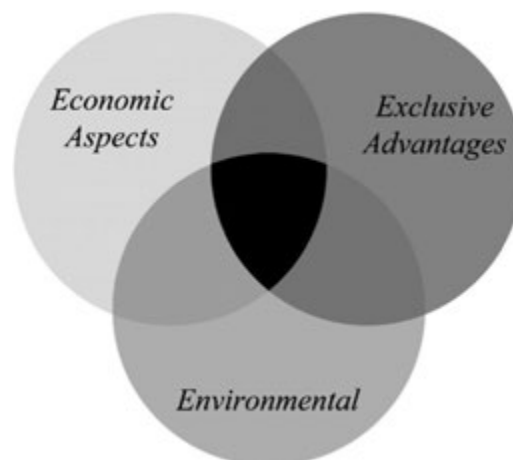


Fig. 1 Schematic of inter-related parameters to consider for each process. Drawn by authors.

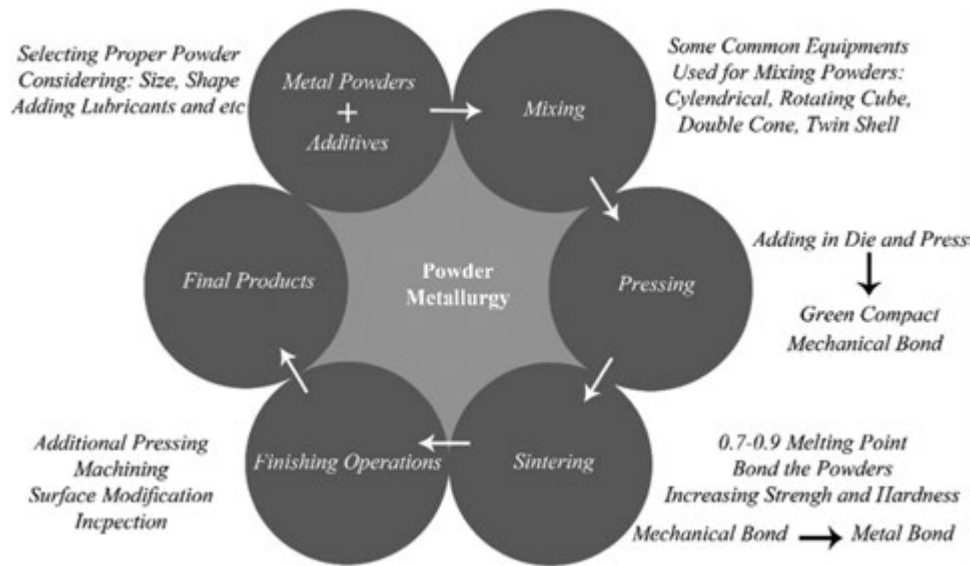


Fig. 2 Graphical overview of the PM production process. Drawn by authors.

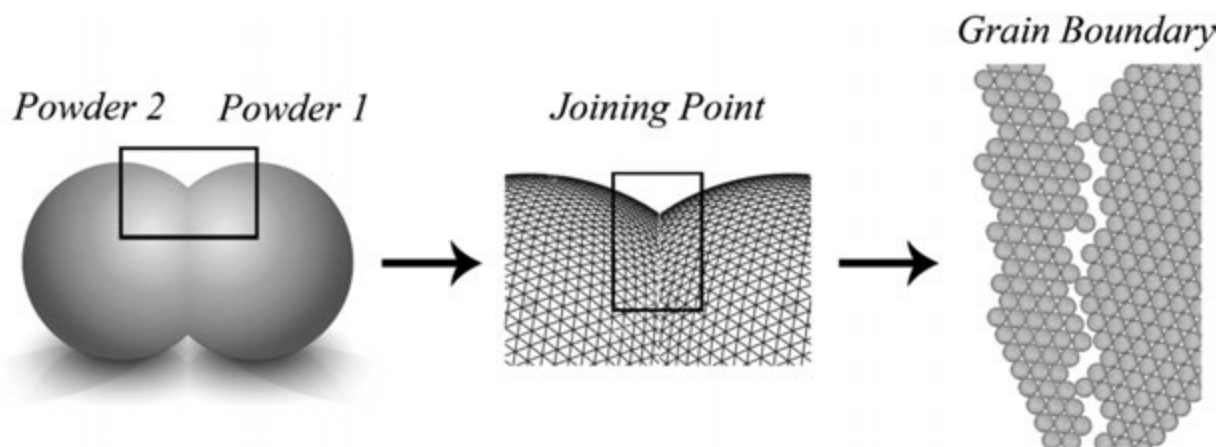


Fig. 3 Powder particle joining process during the PM sintering step. Drawn by authors.

by the selected production process (Höganäs, 2013). Atomization, chemical, and electrolytic processes are three main methods which are used in the mass production of powder materials (Yefimov and Naboychenko, 2009).

In the next step, the matrix powders and strengthening elements are mixed and blended to form a homogeneous combination. MMCs with a matrix of magnesium, aluminum, copper, titanium, or nickel-based superalloys are material systems that have widespread applications in cutting edge areas. These MMCs are reinforced by dispersed particles, platelets, short and continuous fibers (Kaczmar *et al.*, 2000). From this point, the process can be continued via two strategies: cold and/or hot press (sintering) (Pokorska, 2008). Each approach has its own positive and negative points. The sintering process highly depends on the powder size that controls the surface energy in the powders. Smaller particles will result in faster sintering unless there is problematic surface chemistry such as an excessively increased oxide surface area. With the progress of the sintering process at atomic level diffusion, atomic layers build grain boundaries as usual grain boundaries in other production processes (see Fig. 3). If the applied sintering temperature, pressure, and period are long enough, a unified structure without any pores between the powder particles will be produced (Upadhyaya and Upadhyaya, 2011).

PM is an ever-developing method and researchers put effort to open up new activity fields every year (Anniger *et al.*, 2017; Danninger, 2018). One of the characteristics of parts produced with the PM method due to the very high strength materials used is that the parts can be very light in comparison to those produced via other methods (Anniger *et al.*, 2017). This positive point has led to the employment of PM production during the design and production of the next-generation automobiles (Schauerte, 2016).

Also, in some cases, powder metallurgy has improved the synthesis quality of MMCs (Mussatto *et al.*, 2019; Ravichandran and Dineshkumar, 2014; Hamid *et al.*, 2011). For instance, although graphene with remarkable high modulus and high strength is one of the best nominations to be employed as a reinforcement in MMCs, the application of fabricated graphene reinforced MMCs has been restricted due to the difficulty of maintaining the integrity of the reinforcement and achieving bonding with the matrix, both of which

resulted in large scatter in mechanical properties measured experimentally. However recently, research on the synthesis of graphene and reinforced MMCs using the powder metallurgy method, including milling, compaction, extrusion, or rolling, has provided positive results for maintaining reinforcement properties and interfacial bonding (Liu *et al.*, 2016b,c; Tabandeh-Khorshid *et al.*, 2020).

High-Entropy Alloys (HEAs) are one of the groundbreaking research areas in this decade (Li-Sheng *et al.*, 2013; Taylor *et al.*, 2014; Pickering and Jones, 2016; Miracle and Senkov, 2016). Some exceptional studies have proven the efficiency of the powder metallurgy route for producing HEAs (Liu *et al.*, 2016a; Waseem and Ryu, 2017; Eißmann *et al.*, 2017). Regarding this topic, the powder metallurgy proposes numerous advantages for manufacturing high entropy alloys. Using PM methods in the production of HEAs gives the opportunity to avoid casting problems that are caused by the nature of various present materials. Recently, Raza *et al.* (2018) have investigated the effect of aluminum addition on the mechanical properties of CrFeMoV-based quaternary HEA using the powder metallurgy method. They utilized spark plasma sintering (SPS) after planetary ball milling to fabricate AlxCr-FeMoV HEA and found that the yield strength of the alloy at room temperature was increased from 2730 to 3552 MPa with the composition Al_{0.6}CrFeMoV, which included the addition of Al.

Besides these, the HEAs because of their exceptional mechanical properties are employed as reinforcement elements in MMCs (Chen *et al.*, 2015; Karthik *et al.*, 2016; Prabakaran *et al.*, 2017). In an investigation by Chen *et al.* (2015), the PM route was utilized to produce a Cu based AlCoNiCrFe HEAs with very high levels of strength which was well predicted via the viscoelastic Voigt model.

Diffusion Bonding

Joining is an important requirement in the industry (Von Hofe, 2015). It gets more critical in high tech areas which involve novel components and material designs with high precision (Higurashi *et al.*, 2014; Luo *et al.*, 2015). Therefore, it is proper to examine new approaches in their production methods. Assemblies and materials, especially novel ones, can often not be joined by conventional methods. Metal matrix composites, reactive metals, superalloys, optoelectronic and electronic materials (Gosele and Tong, 1998; Shimatsu and Uomoto, 2010; Di Cioccio *et al.*, 2011; Higurashi and Suga, 2016) are some examples where the material benefits are lost by applying the standard joining method. When these joints involve different materials, extra precautions are needed to ensure the required level and accuracy in bond strength can be achieved for the assembly lifetime without negative corrosion or excessive stress levels effects.

Diffusion bonding (Garrett *et al.*, 1966; Dunkerton, 1991) is one process that can be applied to solve these needs in a solid-state manner. The key point for success in bonding processes in solid-state format is removing any barriers on the surface (mainly oxide types) (Shirzadi *et al.*, 2001). As Kazakov (2013) surface oxide hypothesis mentioned: "All metals can be joined if clean surfaces brought together in the range of interatomic forces". The distinguishing point of this joining process is that it can provide joints without detrimental interface features such as oxides, pores, or grain boundary defects. Moreover, diffusion bonding is designed to save the properties of selected base materials which is achieved due to similarity in the physical, phase structure, and chemical properties of the selected materials, see Fig. 4 (Kumar *et al.*, 2019).

Diffusion bonding depends on the quality (smoothness and cleanliness) of the prepared contact surfaces, temperature ($\sim 0.5T_m$), pressure, and time (Kumar *et al.*, 2019). The optimal conditions lead to a homogeneous microstructure with excellent bond strengths. The diffusion bonding can be grouped into three main methods:

(1) Gas Pressure Bonding

In this method, high pressure and elevated temperature are applied and are mostly used for nonmetallic joining, see Fig. 5 (Hodge *et al.*, 1962).

(2) Vacuum Fusion Bonding

For this method, all processes are completed without any intermediate layer in a chamber in low temperatures while a vacuum condition presents with some post-treatments after the first stage, see Fig. 5 (Gösele *et al.*, 1999).

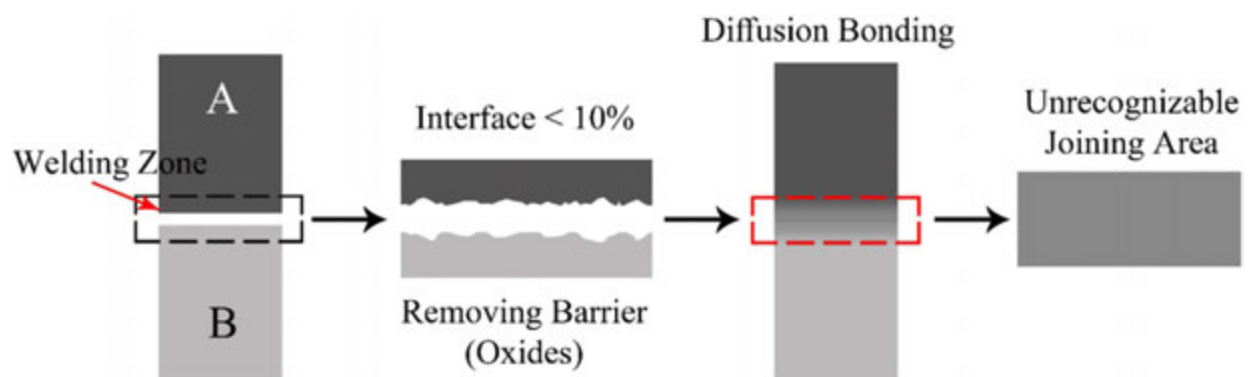


Fig. 4 Schematic of the diffusion bonding process. Drawn by authors.

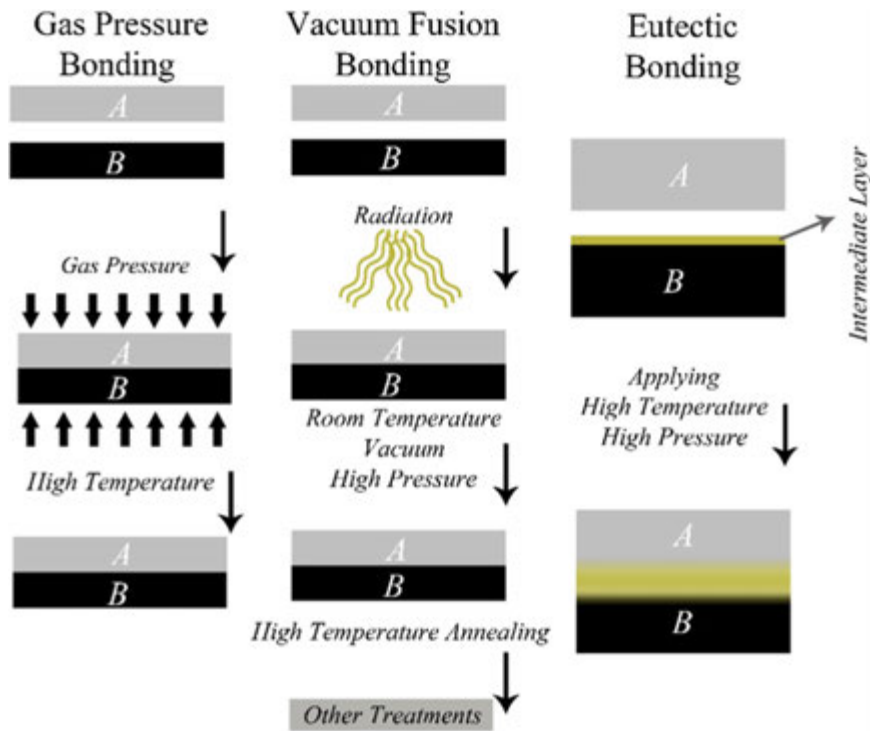


Fig. 5 Schematics of the gas pressure, vacuum fusion, and eutectic-bonding processes. Drawn by authors.

(3) Eutectic Bonding

In comparison to the first two methods, this process possesses low operating temperature and also a deposited intermediate layer to produce a eutectic system. The main idea for a eutectic system is that it has a much lower temperature than the melting temperature of the two base materials, see [Fig. 5](#) ([Schmidt, 1998](#)).

It is known that even with proper surface preparation that the pressure, temperature, and time are most critical for having a proper diffusion process for bonding. Neglecting these factors can affect the process and can result in undesirably weak bonding ([Ramm et al., 2011](#)).

In general, the diffusion bonding method possesses unique and distinguishing characteristics that make this joining method the only accessible way in the production of ultra-precision devices in cutting edge areas such as the production of optoelectronics, MEMS, NEMS, and semiconductors.

Different studies have been conducted to achieve the optimum parameters of diffusion bonding for various materials ([Basuki et al., 2012](#); [Singh et al., 2016](#); [Lee et al., 1999](#)). For instance, the effect of duration in diffusion bonding (using low vacuum technique) of Mg_2Si reinforced aluminum metal matrix composite (MMC) using Cu interlayer at $540^\circ C$ has been investigated by [Nami et al. \(2010\)](#) in which the properties are greatly improved over those of pure aluminum sintering ([Liu et al., 2019](#)). They have used an MMC manufactured by an in situ production method containing 15% Mg_2Si revealing that the shear strength of joints improved with increasing the duration of diffusion bonding up to 150 min. This was attributed to the dissolution of the earlier diffusion films appearing in the elimination of the $CuAl_2$ layer.

Forging

Forging is a group of manufacturing processes that involve hammering, pressing, and rolling. The force is applied to shape the metal near the net-shape geometry. It is one of the oldest manufacturing processes from ancient times which started by hammering bronze by hard stones. This process can be categorized based on the forming temperature as cold, warm, and hot forging ([Gronostajski et al., 2019](#)). Each approach has its advantages and disadvantages which will be discussed in the next sections.

Cold Forging

This forging method operates in the range of room temperature to below recrystallization temperature with high materials conservation. Being under recrystallization temperature gives the ability for causing oriented structure (texture) in the end products. Moreover, cold forging with huge plastic deformation can be offered as an accurate process with a well surface finish.

However, it requires high press levels which can result in extra treatment steps and higher forces on equipment (Bay, 1994; Groenbaek and Nielsen, 1994; Sedighi and Mahmoodi, 2009; Miura *et al.*, 2014).

Warm Forging

Warm forging processes take place around recrystallization temperature between the cold and hot forging processes with the presence of lubricants as additives. This method possesses higher temperatures which require lower pressure levels and eliminates extra treatment steps. In general, this approach is a combination of both cold and hot forging process with their advantages and disadvantages (Sheljaskov, 1994; Neugebauer *et al.*, 2001).

Hot Forging

If the working temperature passes the recrystallization temperature to higher amounts, forging can result in different outcomes from previous methods. This process gives the ability to forge larger parts because of greater ductility, which mentioned previous approaches are unable to perform. Besides, the microstructure needs the least amount of post-treatment processes. But, working in high temperature beside its positive points, has negative points like decreasing tool life, low accuracy, and poor surface finish (Hoffmanner, 1971; Mcqueen, 1984; Mcqueen and Kassner, 2005).

Every working condition in forging processes have both advantages and disadvantages (Senkov *et al.*, 2006). Therefore, a delicate balance should be created between needs and processes. In simple words, if all points put together, some general trends can be drawn and gives perspective to choose the most appropriate process.

In general, with shifting from cold forging to hot forging:

- (1) Formability increases.
- (2) Accuracy decreases.
- (3) Pressure decreases.

Hammering, pressing, and rolling can be done in two die types: open and closed die see Fig. 6. Each has its advantages and disadvantages which will be discussed in the next paragraphs.

Open die forging processes are highly recommended in the manufacturing of very large parts with considering designed microstructural properties (Nisbett, 2005). Large manufactured parts with highly limited production methods like the power industry crucially depend on the open die forging method (Hoffelner, 2013). By the progress of industry and entrance of new materials, the need for process monitoring in every single moment of production in open die forging is desirable (Ma and Tian, 2014; Hawryluk *et al.*, 2017). Therefore, improving the mentioned ability is the next challenge for this method and requires detailed research in this area.

On the other hand, close die forging processes are proposed for manufacturing small parts with desirable texture for special purposes. This method can be used in mass production with the least post-treatments and machining processes. In other words, closed die forging employed for the precision forging of products with near details to final shape.

The MMCs spread out in different areas and their final properties determine the manufacturing method to choose. The forging method in the production of MMCs mostly used in automobile and aerospace areas with high mass production (Lee *et al.*, 2001; Jiang *et al.*, 1995; Purohit *et al.*, 2017). For instance, closed die hot forging has been used to produce a connecting rod of an

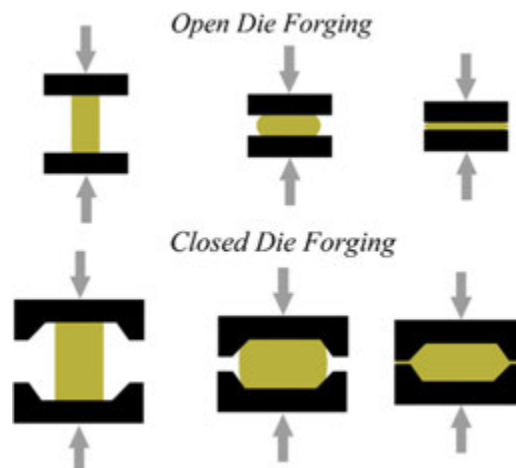


Fig. 6 Schematic for: Open and Closed Die Forging Processes. Drawn by authors.

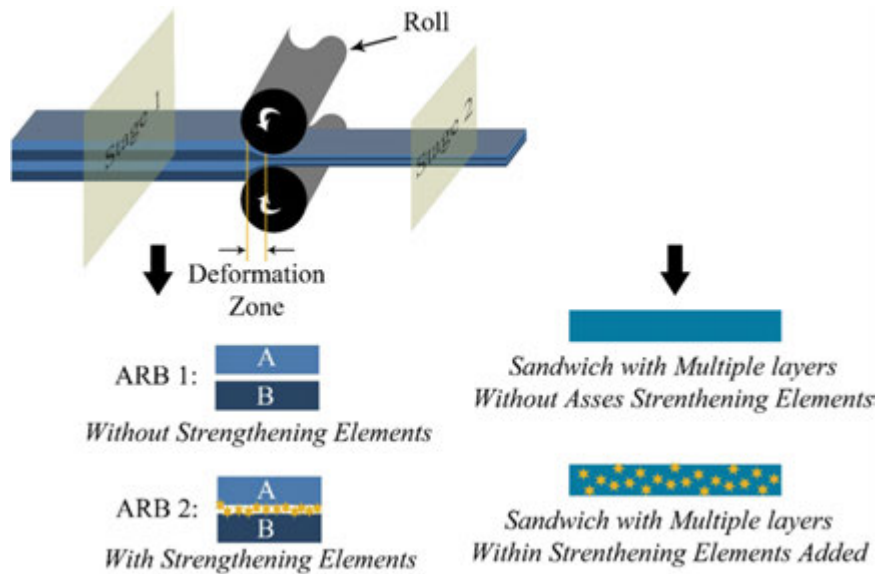


Fig. 7 Schematic of the accumulative roll bonding process. Drawn by authors.

automobile engine using AZ80 magnesium alloy and SiC reinforced ZC71 MMC (Kevorkijan, 2003). Furthermore, the microstructure and mechanical properties of hot forged and extruded samples were studied and considerable weight reduction was obtained after redesigning and substituting the material with magnesium-based MMC.

Accumulative Roll Bonding (ARB) Process

This manufacturing method is a well-known technique in metal matrix composites production (Ghalehbandi and Malaki, 2019). The recent development of the ARB process has focused on achieving nanostructured and ultra-fine grained metal matrix composites from multiple rolling passes (Saito *et al.*, 1999). This process is performed with and without the presence of strengthening elements in the structure, see Fig. 7.

With the presence of strengthening elements of different shapes, distribution, and type, the resulting composite possesses a combination of metallic properties (ductility and toughness) and ceramic properties (high strength and modulus) (Jamaati *et al.*, 2011; Reihanian *et al.*, 2012). As a recent development, Carbon Nanotubes (CNTs) have received attention because of their potential to provide significant strengthening (Hidalgo-Manrique *et al.*, 2019; Naseer *et al.*, 2019).

Nanostructured MMCs possess high-strength, formability, hardness, and ductility. A key feature of this process is the application of severe plastic deformation (SPD) (Cao *et al.*, 2018) in rolling on fixed dimensional rolled materials (Azushima *et al.*, 2008; Harsha *et al.*, 2018). In general, the accumulated plastic strain level during the ARB method is higher than other MMC production processes such as extrusion and forging.

In the ARB method, multiple rolling processes are applied. By doing so, ultra-fine grains can be produced within the final product. In the process, first, surfaces are cleaned from impurities (oxides and oils). Then the permanent layers are rolled and are cut to the initial dimension required for the next stage. After a further cleaning step, the thus prepare sheet is rolled like in the first cycle, a process which is repeated in subsequent rolling cycles, see Fig. 8 (Azushima *et al.*, 2008; Tsuji *et al.*, 2003).

This method enables the mass production of composites with nanostructured grains and excellent mechanical and physical characteristics (Reihanian *et al.*, 2016).

Different types of materials have recently been applied as the reinforcement material of the composites fabricated with the ARB process. For instance, Alizadeh *et al.* (2019) have successfully fabricated E-glass fibers reinforced aluminum MMC using the cross accumulative roll bonding (CARB) process. As shown in Fig. 9, although porosities and discontinuities between the Al layers have been observed after the first pass of ARB, a homogenized distribution of fibers was achieved after eight cycles. It was also reported that the addition of E-glass fibers increases surface and bulk mechanical properties such as ultimate strength and hardness, with a corresponding reduction in the ductility of the fabricated MMC.

In another work, high-strength Al based MMC with anodized alumina and zirconium carbide reinforcement was produced using the ARB process (Shamanian *et al.*, 2015). Noticeable enhancement in particle distribution and uniformity of reinforcement with an increased number of ARB cycles were demonstrated. Moreover, an inspection of the tensile test results revealed that the composites have a better elongation and tensile strength compared with the starting aluminum strips. Also,

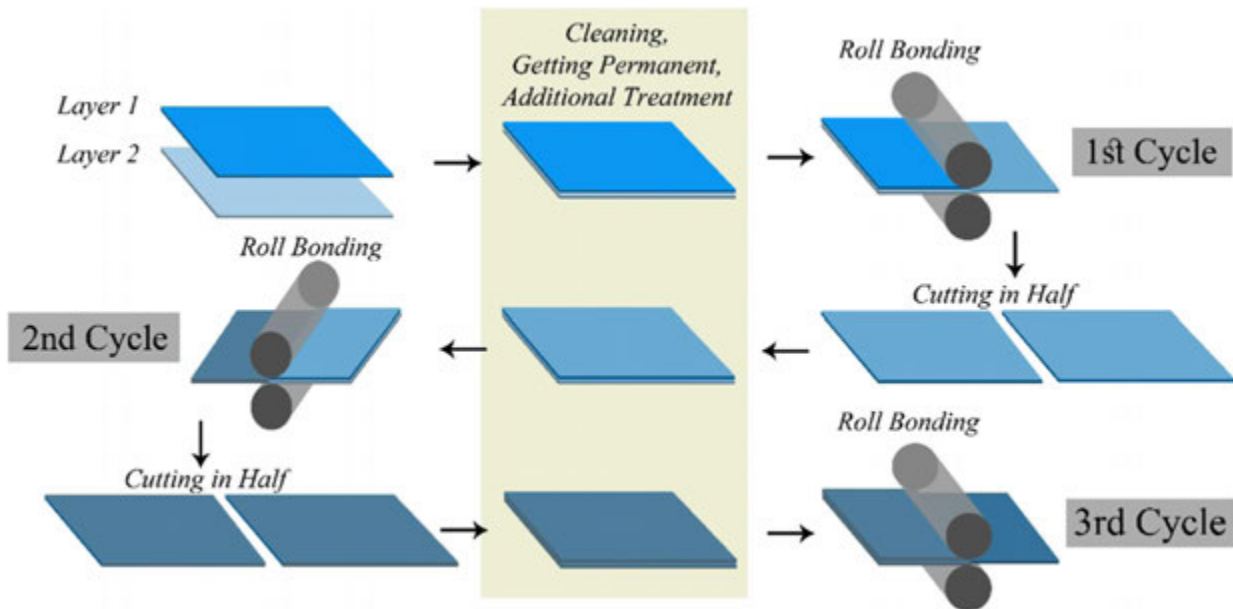


Fig. 8 Schematic of the methods for multiple passes within the accumulative roll bonding process. Drawn by authors.

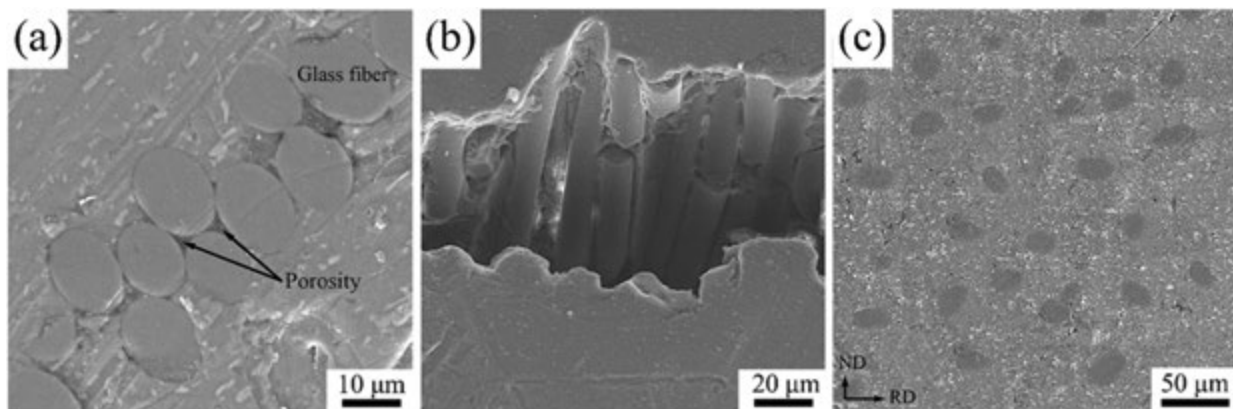


Fig. 9 SEM of the E-glass fiber reinforced MMC fabricated by ARB: (a) After the first cycle, (b) the detachment of Al layers in the presence of the fibers at the first cycle, (c) the distribution of the E-glass fibers in the metal matrix after the eight cycles. Reproduced from Alizadeh, M., Shakery, A., Salahinejad, E., 2019. Aluminum-matrix composites reinforced with E-glass fibers by cross accumulative roll bonding process. *Journal of Alloys and Compounds* 804, 450–456.

the effect of ARB cycles on the microstructure evolution and mechanical properties such as microhardness, tensile, and fatigue performance of the Al2024/Al6061 composite has been investigated by Dhyai *et al.* (Jawad *et al.*, 2019). They successfully fabricated the Al2024/Al6061 laminated composite using the ARB process with the various number of passes, see Fig. 10.

Extrusion

Extrusion is a manufacturing process that can be conducted in various ways for different resulting geometries and is classified in three main branches and six sub-branches, see Fig. 11. This production process crucially depends on the plastic deformation of raw materials. In general, extrusion is about forcing a block of raw material through a solid die to take a final sought shape though material dimension reduction and elongation (Davis and Semiatin, 1996).

As demonstrated in Fig. 12, during the process the raw materials can be formed from the system by two different methods, in the same direction, and along the reverse direction compared to the forming die movement.

In addition, extrusion like other manufacturing processes can be done in a variety range of temperatures. The hot extrusion typically takes place at and over $0.5T_m$ (melting temperature) of the extruded materials. This high working temperature beside

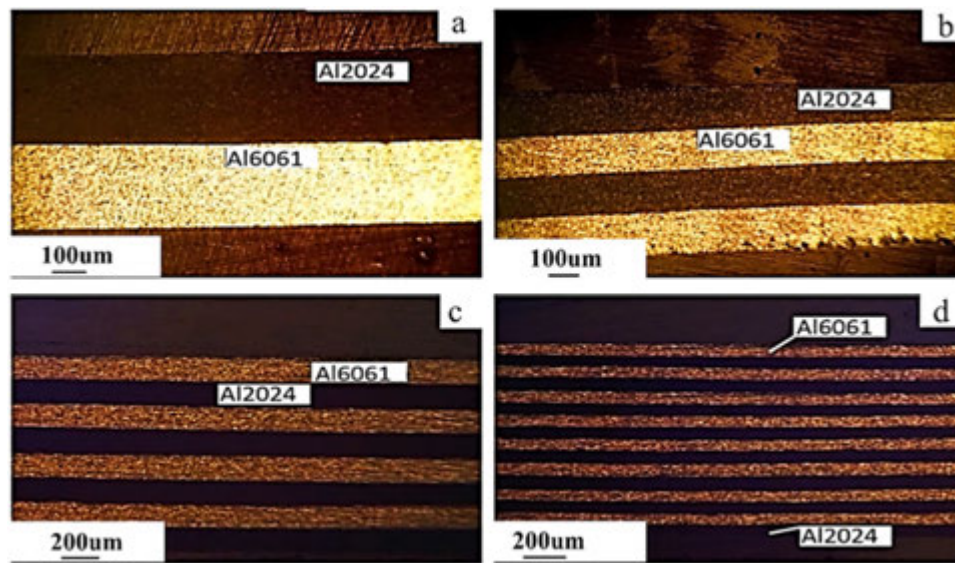


Fig. 10 Optical micrographs of the Al 2024/Al 6061 composites after (a) 1 cycle, (b) 2 cycle, (c) 3 cycle, and (d) 4 cycles. Reproduced from Jawad, D.H., Hosseinzadeh, A., Yapici, G.G., 2019. On the mechanical behavior of accumulative roll bonded lightweight composite. *Materials Research Express*, 6.

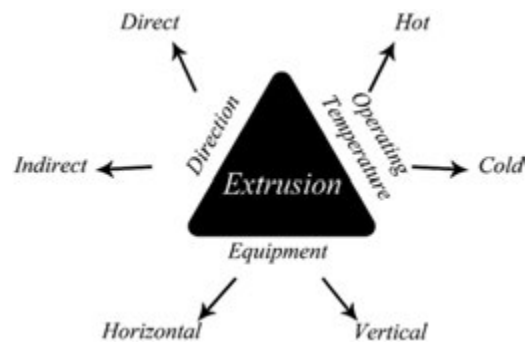


Fig. 11 Classification system for the extrusion process. Drawn by authors.

huge pressure can be detrimental for the extrusion die surfaces and can result in costly repairs. Therefore, the choosing of a correctly functioning lubricant for evading this damage is important.

On the other hand, performing the process at room temperature which is known as cold forging, can result in a much better surface finish without any oxidation side effects. In general, extrusion can be thought of as a branch of forging. Thus as mentioned before in forging, similar advantages and disadvantages can also be cited for the extrusion process.

The different extrusion methods besides producing profiles in various forms can be used in the manufacturing of MMCs which are employed in cutting edge areas. The extrusion process can also be employed in the manufacturing of metal matrix composites such as wire for magnet applications (Hishinuma *et al.*, 2019a,b) and superconductors (Barannikova *et al.*, 2019; Zhang *et al.*, 2019). The production in these MMCs usually includes two main steps of monofilament bar fabrication and multifilament bar/wire fabrication (Zhang *et al.*, 2019). The schematic of the aforementioned process is illustrated in Fig. 12.

Deaquino-Lara *et al.* investigated the microstructural and mechanical characteristics of Al7075-graphite composites produced by the hot extrusion method. The specimens with different graphite contents were manufactured and milled before the extrusion process. It was reported that despite the homogeneous dispersion of graphite, a particular amount of carbide was crystallized. It was also found that the grain size decreases with the increase of milling duration. Moreover, the duration of milling and the amount of graphite were tuned within the range examined for improved mechanical properties positively (Deaquino-Lara *et al.*, 2015).

Equal channel angular extrusion (ECAE) as a modified version of conventional extrusion can apply a large amount of plastic deformation on the material without changing the cross-section area. In the last two decades, ECAE has been examined to enhance the mechanical properties of MMCs (Miranda *et al.*, 2018, Li and Huang, 2014, Yapici *et al.*, 2004, Huang *et al.*, 2015, Zheng *et al.*, 2005). For instance, recently Huang and Ali (2019) investigated the influence of SPD performed by ECAE on the microstructure,

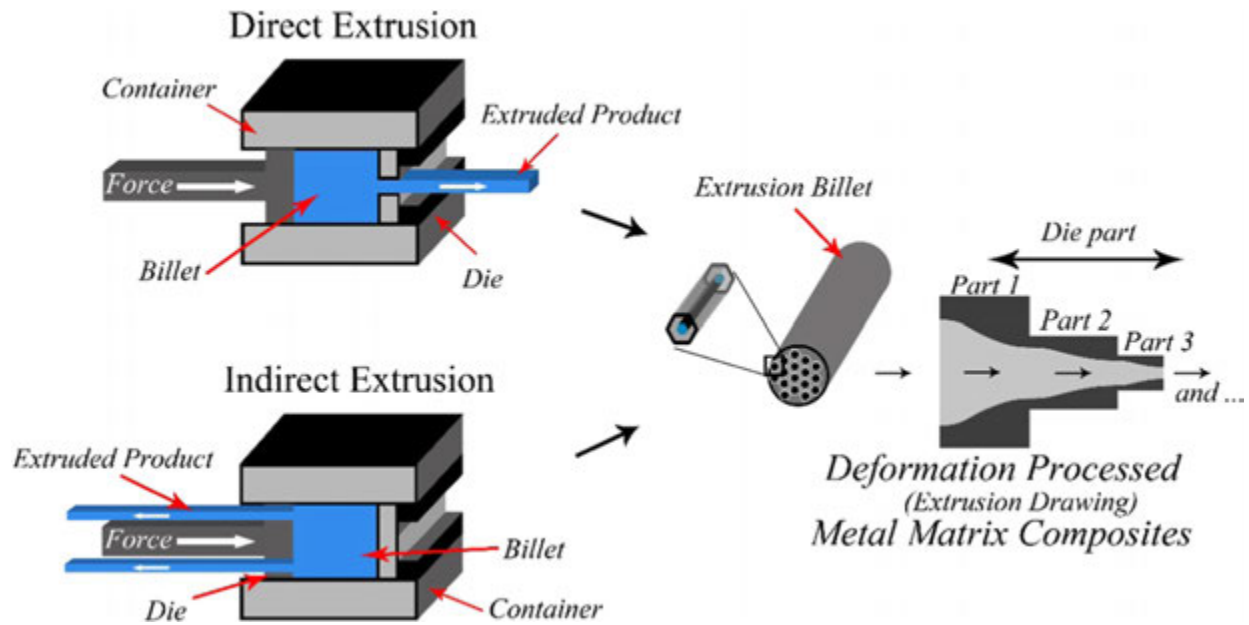


Fig. 12 Schematic of the direct and indirect extrusion methods. Drawn by authors.

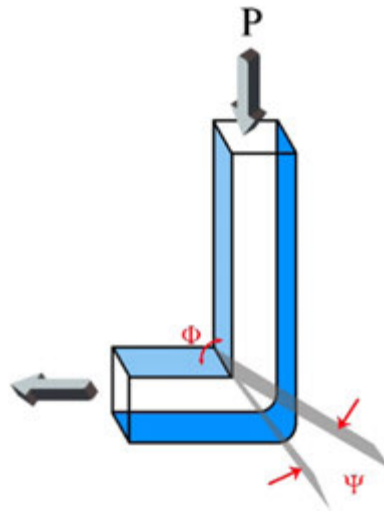


Fig. 13 Schematic of the equal angular extrusion (ECAE) process. Drawn by authors.

reinforcements distribution, and mechanical properties of AZ61/SiC MMC. They reported that homogeneous grains and segregation of SiC reinforcements along the grain boundaries were achieved by increasing the number of ECAE passes. Moreover, they found that SiC/AZ61 MMC with 2 wt% SiC demonstrated the highest strength, ductility, and strain hardening rate after ECAE processing (Fig. 13).

Explosive Bonding

This method is another solid-state bonding method for producing a composite metal matrix involving similar and dissimilar materials (Shu *et al.*, 1995). In this approach, the top layer is impacted with high pressure and hit the bottom layer at high speed which leads to a clean metallurgical bond. This process employs explosive force that in most cases is over 45 GPa. These conditions lead to high levels of plasticity in the solid material, eliminating the need for liquid state processing. Explosive bonding can, therefore, be used for the production of exclusive composites (Carpenter, 1981). These characteristics make the process

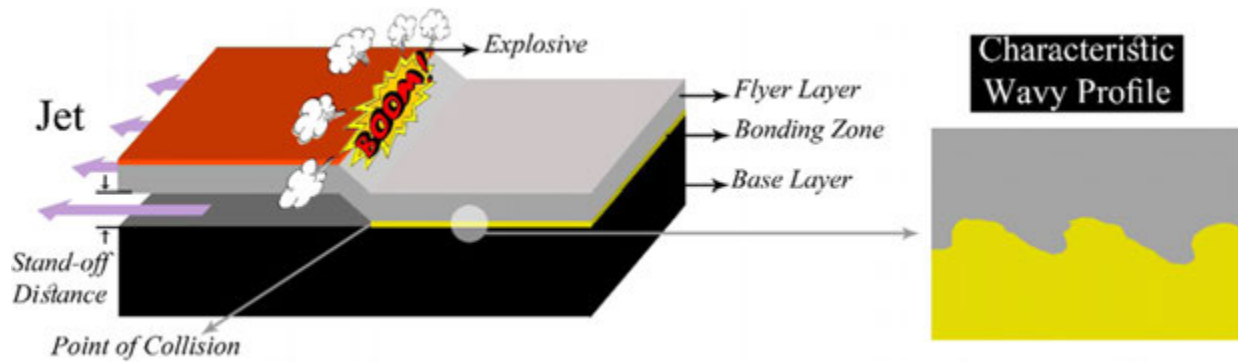


Fig. 14 Schematic of the explosive bonding process. Drawn by authors.

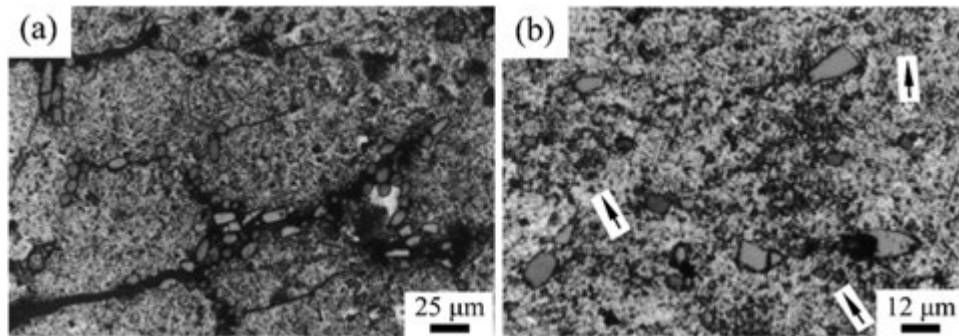


Fig. 15 Explosive bonding of carbon fiber MMC with (a) fiber agglomerations resulting from the hand-mixing preparation, and (b) fiber particulate in ball-mill mixed compacts. Reproduced from Raghukandan, K., Hokamoto, K., Lee, J.S., Chiba, A., Pai, B.C., 2003. An investigation on underwater shock consolidated carbon fiber reinforced Al composites. *Journal of materials processing technology* 134 (3), 329–337.

appropriate for producing components used in high temperature and cryogenic applications, electrical applications, and aggressive environments (Crossland, 1976; Blazynski, 1983; Alymov and Golosova, 2018).

The explosive bonding process includes several steps which are packing (setting the backer and the cladder), determining the velocity and quantity of explosion based on process, and structuring. With the start of the bonding process and collision of two layers, a plasma jet is produced that removes oxides and any other impurities from the surface and at a fraction of a second subsequently bonds the layers, see Fig. 14 (Crossland and Bahrani, 1968; Crossland and Williams, 1970).

As mentioned previously this process can be employed in the production of solid-state metal matrix composites. In this process, high pressure and velocity of the shockwave caused by explosive designation are employed to compact the powders (shock compression processing). It is quite infeasible to use conventional powder processing methods to synthesize MMCs with very hard materials (metal and ceramic powders). This approach is a unique way in which these materials could be formed jointly (Thadhani, 1988; Eakins and Thadhani, 2009).

Raghukandan *et al.*, 2003 applied a high explosive underwater shock wave technique with a detonation velocity of 6.9 km s^{-1} to consolidate a carbon fiber reinforced MMC. They compared the homogenization of reinforcements in the composites after hand-mixing and ball-mill mixing. As shown in Fig. 15, while many porosities, reinforcement agglomeration, and cracks were observed in the hand-mixed MMC, a uniform distribution of fibers without cracks and agglomeration of particles were achieved after the ball-mill mixing.

Friction Stir Processing (FSP)

Recently, the fabrication of particle reinforced MMCs using the friction stir processing (FSP) method has received significant interest from the research community (Deepan *et al.*, 2017; Naser and Darras, 2017; Sahraeinejad *et al.*, 2015; Narimani *et al.*, 2016; Nandan *et al.*, 2008; Mishra and Ma, 2005; Paidar *et al.*, 2019; Heidarzadeh *et al.*, 2018). FSP is based on the fundamentals of friction stir welding (FSW). It can be used for the modification of as-cast structures and for the production of MMCs. During FSP, a rotational tool is inserted into the material and then is traversed along the processing line. To produce MMCs, before FSP, secondary phase particles or the reinforcement phase are injected into the material via grooving or drilling. Then the injected reinforcement is impacted into the grooves or drilled impressions. The severe plastic deformation and heat generated by the

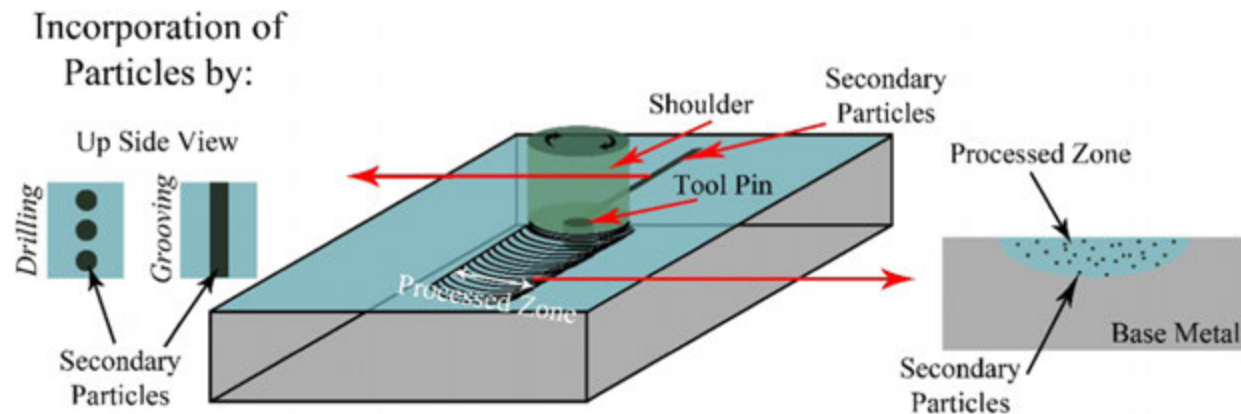


Fig. 16 Schematic of the friction stir processing production of a metal matrix composite surface. Drawn by authors.

rotational tool causes the distribution of the reinforcement into the metal matrix, which results in the MMCs, as shown schematically in Fig. 16. For instance, Hosseinzadeh *et al.* enhanced the microhardness of Al2024 up to 50% by embedding SiC particles into the Al matrix. They found that the addition of SiC reinforcements enhanced the yield strength of the as-received Al form about 120 MPa up to 320 MPa due to the grain refinement and Orowan strengthening throughout the FSP section. Furthermore, they investigated the high-temperature tensile behavior of Al2024/SiC MMC and the strain rate sensitivity of fabricated composite (Hosseinzadeh and Yapici, 2018).

Summary

In this article, different solid-state methods for the production of metal matrix composites were presented including powder metallurgy, diffusion bonding, forging, accumulative roll bonding, extrusion, explosive bonding, and friction stir processing. Detailed process schematics were used to explain the mechanisms that provide the formation of a composite structure. All of the solid-state methods presented typically result in superior microstructure and mechanical properties compared to those of liquid state processing methods. For each of these processes, to obtain improved properties, it is very important to optimize and control the process parameters and to select the right base materials and reinforcements.

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Green Materials and Production of Metallic Composite Materials

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Glossary

Agro-industrial wastes Cheapest and abundantly available natural carbon sources such as sugarcane bagasse, wheat bran, rice bran, corn cob, and wheat straw.

Fly ash During the combustion process, the volatile matter and carbon burn off, and the coal impurities, such as clays, shale, quartz, and feldspar mostly fuse and remain in suspension. These particles are carried along with the flue gas. As the flue gas approaches the low temperature zones, the suspension forms predominantly into spherical particles which are called fly ash.

Green materials Defined as materials that are non-toxic, improve occupancy health, lower cost, conserve energy and water use, and reduce waste products.

Recyclable materials Defined as materials that can move from being waste material to being reused through reprocessing or re-purposing.

Reinforcement Materials which are stronger and stiffer than the matrix.

Sustainability Means meeting our own needs without compromising the ability of future generations to meet their own needs. In addition to natural resources, we also need social and economic resources. Sustainability is not just environmentalism. Embedded in most definitions of sustainability we also find concerns for social equity and economic development.

Introduction

Metal matrix composites (MMCs) are used in various engineering applications such as aircraft structures, automobile structures, vehicle drive shafts, and automotive pistons. The advantages of MMCs are their light weight, high specific strength, high thermal conductivity, excellent wear, and corrosion resistance. As global societies go on to grow, increasing attention is being given on ensuring the sustainability of applied material systems. Topics such as embodied energy, greenhouse gas emissions, toxicity, and resource depletion are being examined more and more by material producers. Improving the sustainability of material systems will need not just the development of new sustainable materials, but also the increased application of existing green materials. Also, the ever-increasing demand for low cost reinforcement encouraged the interest toward production and utilization of by-products from industry as reinforcements since they are readily available or are naturally renewable at affordable cost. One existing class of materials with good environmental character are green composites. Green composites are defined, in this article, as metal matrix composites reinforced with waste or recycling materials such as fly-ash, red mud, rice-hull ash, bagasse ash, basalt fiber, breadfruit seed hull ash, maize stalk waste, and eggshells waste particle. A lot of environment pollution due to the waste of industries/societies encourages our societies for utilizing these waste products in research and technical areas. These raw materials offer great opportunities because synthesized reinforcements can be produced in situ economically. Green composites derived from renewable resources bring very promising potential to provide benefits to companies, natural environment, and end-customers due to the associated decreased usage of petroleum resources. The shift to more sustainable constructions in the automotive industry is not only an initiative toward a more viable environment and cost efficiency but also is demanded via European regulations. The latter are playing an important role as a driving force toward sustainable materials' use. According to the European Guideline 2000/53/EG, 95% of the weight of a vehicle is be recyclable by 2015 ([Greening transport, European commission, 2008](#)). One of the best ways to balance cost and sustainability is with the use of composites in automobile panels, as introduced by a number of automakers who use renewable materials in composites. Composites made of renewable materials have been extensively used in auto-body parts.

Materials experts from various automakers estimate that an all advanced composite auto-body could be 50%–67% lighter than a similarly sized steel auto-body as compared with a 40%–55% mass reduction for an aluminum auto-body and a 25%–30% mass reduction for an optimized steel auto-body ([Davies, 2003](#)). Specifically, for the future electrical vehicle, the light weighting materials approach is vital in order to offset the added weight of batteries while at the same time lowering the weight and increasing their maximum range. Such an auto-body could be even lighter with the addition of natural reinforcements in the composite because these are less dense than synthetic types. With development of the stir casting process which is a cost-effective method for manufacturing composites it is relatively easy to develop and produce advanced green metallic composites. There are some recently published papers on green metal matrix composites and this article provides a concise summary of developed green metal matrix composites.

Green Materials

The development of advanced composite materials having superior mechanical properties has opened up new scope for engineering component and product designs. Advantages including improved corrosion resistance, electrical insulation, easy of processability with lower forming energy requirements, lower tooling and assembly costs, higher stiffness and strength, fatigue resistance and lower weight than metal alternatives. These have made composites widely acceptable in structural applications. The so-called advanced composites have replaced metals because of their excellent mechanical properties and low density giving them high specific strength and stiffness. Such weight savings are highly desirable for applications in transportation to reduce weight and associated fuel consumption.

Physical and mechanical properties of composites depend on the properties of the constituent materials, i.e., the matrix and reinforcement. The strength and stiffness of the composites are directly a function of the reinforcement properties which carry most of the load and their volume content. The reinforcement helps to maintain the relative position of the reinforcement within the composite and, more importantly, transfers the load from the bottom reinforcement to the intact reinforcement. As a result, matrix/reinforcement interfacial properties are also important and have a significant effect on composite properties including toughness and transverse fracture stress. To fabricate high strength composites, all three factors namely reinforcement properties, matrix properties as well as matrix/reinforcement interface characteristics are critical. Currently most of the reinforcements are derived from petroleum feed stocks and do not degrade for several decades under normal environmental conditions. Composites made from synthetic reinforcements cannot be reprocessed or recycled. In addition, at the present rate of consumption, the world petroleum resources are estimated to last for the next 50 years. Thus, there is a great interest generated in developing green composites using fully sustainable, biodegradable, environment friendly, and annually renewable reinforcements, particularly those derived from plants. A variety of reinforcements such as snail shell, waste eggshells fly ash, etc., have been used to fabricate green composites for many applications. Thus, researchers are now focusing on the use of green products as an alternative source of reinforcement materials in the composite production at low costs.

Development of Green Metal-Matrix Composites from Industrial/Agricultural Waste Materials

Metal matrix composites (MMCs) usually consist of a low-density metal such as magnesium or aluminum reinforced with particulate or fibbers of a ceramic material, such as silicon carbide or graphite. Metal matrix composites such as Al6000 series (Al6061/6063) are of great interest in industrial applications where they are lighter with high specific strength, stiffness, and heat resistance. Fig. 1 compares the cost breakdowns of a component manufactured from steel and discontinuously reinforced aluminum (DRA) composite alternative. For the steel part, the cost of the input material is a relatively small fraction of the total part cost, while the cost of the input DRA constitutes a much higher percentage of the final cost. Moreover, the cost due to machining, both variable and capital, can also be a significant percentage of the final part cost. Because the automotive industry is oriented toward high-volume production, capital investments can be extremely large and, in many cases, a limiting factor. As an example, the capital required for a transfer line to machine a single, relatively simple component such as a connecting rod can easily exceed \$20 million when production volumes of 250,000 to 500,000 automobiles are considered. Manufacturing methods, including machining, that provide efficient shape fabrication are integral in analyzing the costs and benefits of MMC components.

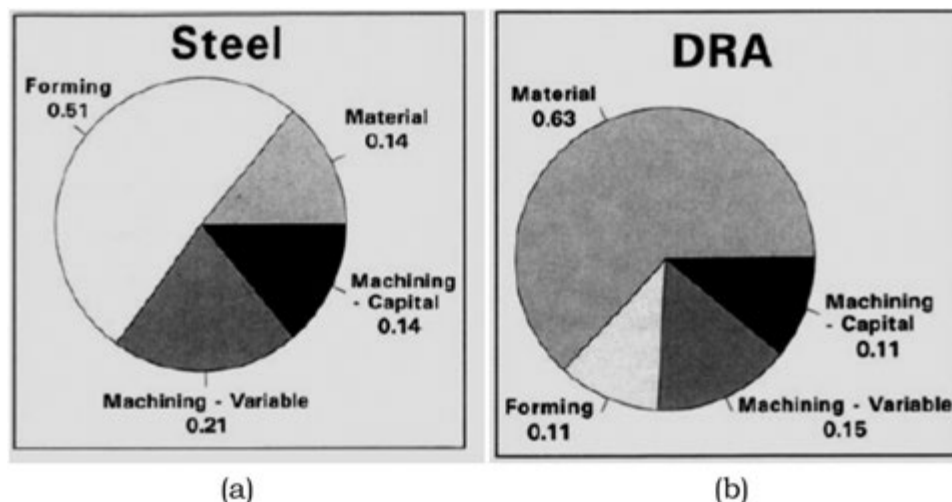
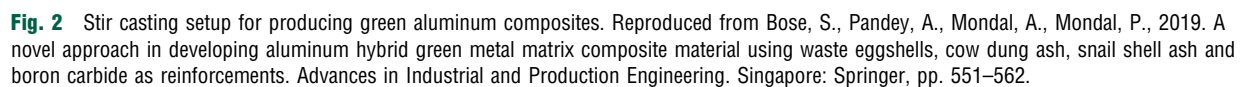


Fig. 1 The proportions of the various costs in a typical automotive component manufactured from (a) steel and (b) discontinuously reinforced aluminum. Reproduced from Allison, J.E., Cole, G.S., 1993. Metal-matrix composites in the automotive industry: Opportunities and challenges. JOM 45 (1), 19–24.



The 6000 series of aluminum alloys exhibit very high mechanical properties, formability, higher corrosion resistance, better weldability, high strength-to-weight ratio, and a lower cost as compared to other counterparts, such as the 2000 and the 7000 series. This series of aluminum alloys constitutes the highest volume of aluminum products, which have been widely employed in a variety of technologies, including automobile and aerospace industries, pipes, architectural applications, bicycle frames, transportation equipment, bridge railings, and welded structures. Among the vast variety of alloying elements available for the development of the heat-treatable 6000 series, recent investigations have proposed silicon and magnesium as the major alloying elements. Moreover, both elements are essential materials for precipitate strengthening (SreeAravind *et al.*, 2019; Zhao *et al.*, 2019; Vazdirvanidis *et al.*, 2019). Furthermore, aluminum AA6063 alloy is widely employed for construction and transportation applications (Thamizhvalavan *et al.*, 2019). Due to the rapid industrial and technological growth, given the opportunities for various applications, economic, and environmental benefits, it is becoming increasingly important to develop material that will have a good strength-to-weight ratio suitable for automotive, aerospace, and defense applications from industrial, agro, and bio-waste resources (Bose *et al.*, 2019). These properties are easily achievable with the aluminum alloy based metal matrix composite (AMC) at lower costs (Joseph and Babaremu, 2019; Magibalan *et al.*, 2018). The fabrication of an enhanced composite material can be achieved through the careful selection of reinforcement materials having modulus and stiffness which are higher than the base metal or alloy materials (Potluri, 2019). Hence, the reinforcement material must have a higher strength and hardness value compared to the continuous soft ductile nature of the matrix phase. Now much more emphasis is given to develop lighter materials using green and low cost reinforcements. Based on the use of agricultural and industrial waste materials, the composites are categorized into three groups. (1) Composites having waste materials as matrices, (2) Composites in which the reinforcements are waste materials, and (3) Composites in which both, the matrix and the reinforcement, are waste materials. This categorization is shown in Fig. 3.

The agro-based industries generate a significant amount of industrial waste (fly-ash) and agro-waste materials such as sugar cane, bagasse ash, coconut ash, bread fruit hull ash, groundnut husk ash, maize husk, and rice husk ash. Their suitability as

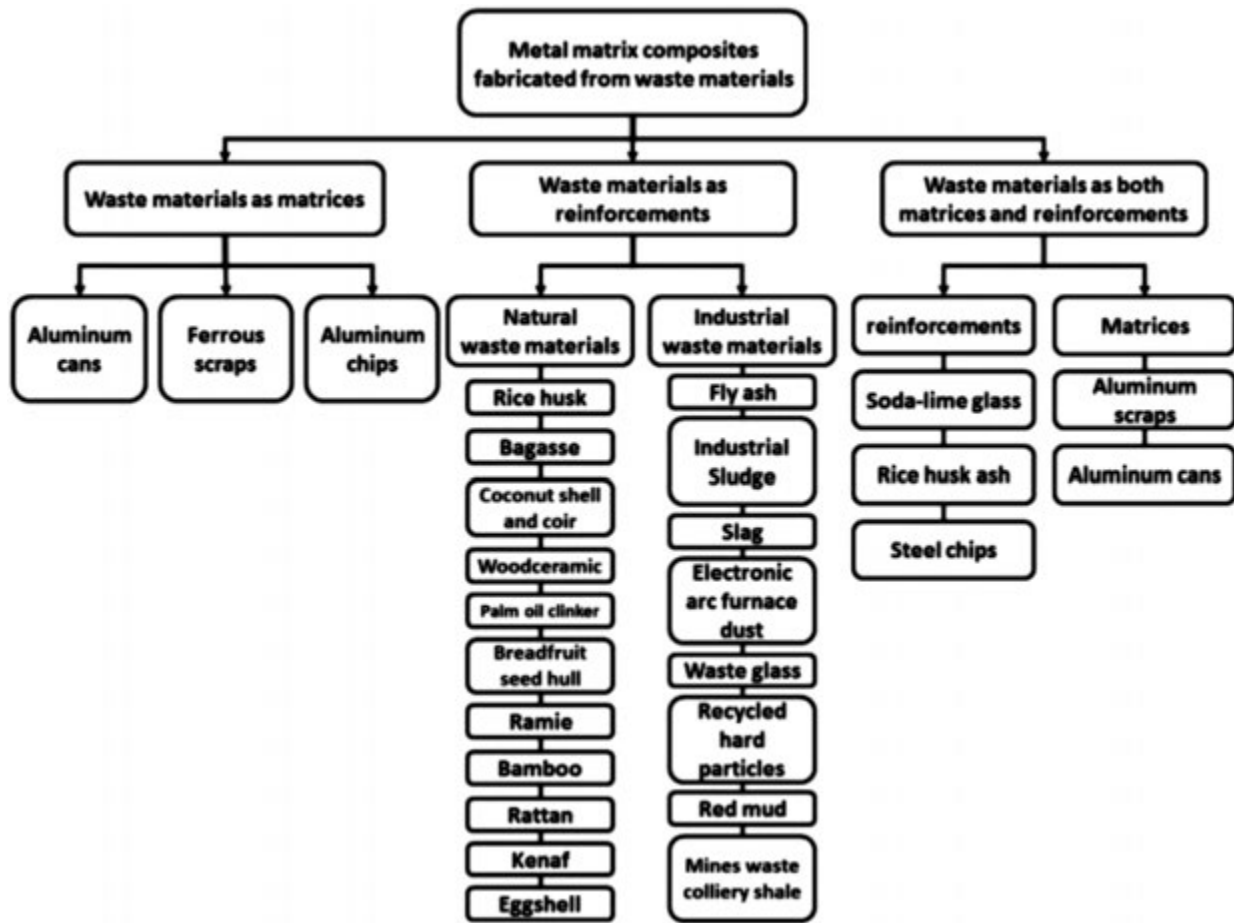


Fig. 3 Classification of metal matrix composite materials fabricated from waste materials. Reproduced from Bahrami, A., Soltani, N., Pech-Canul, M.I., Gutiérrez, C.A., 2016. Development of metal-matrix composites from industrial/agricultural waste materials and their derivatives. *Critical Reviews in Environmental Science and Technology* 46 (2), 143–208.

reinforcement materials in metal matrix composites have been reported extensively due to the presence of hard phase substances with lighter density characteristics as well as the capability to withstand higher temperature conditions. The major constituents of industrial- and agro- waste ashes are SiO_2 , Al_2O_3 , and Fe_2O_3 . Al–Si–Fe alloy matrix composites reinforced with breadfruit seed hull ash particles were fabricated through the double stir casting method and the effect of weight fraction of green reinforcement on the microstructure and mechanical properties was studied (Atuanya *et al.*, 2012). Microstructure studies revealed that with an increase in weight fraction of reinforcement, the matrix grain size decreased and the mechanical properties were improved. Importantly, fractography studies showed that fracture initiation does not occur at the particle–matrix interface (Atuanya *et al.*, 2012). Breadfruit seed hull ash contains hard phase substances suitable for reinforcement within the metal matrix composites with high thermal resistance properties and offer a potential candidate for automotive applications. A similar result was obtained by Madakson *et al.* (2012) using coconut shell ash. A green aluminum matrix composites reinforced with 15% coconut shell ash (with size of 60 μm) was produced by Kumar (2016). The average density of aluminum–coconut shell ash composite is less than conventional aluminum alloy. The presence of hardening substances like SiO_2 and MgO in the reinforced material increases the hardness of aluminum–coconut shell ash composite.

In a similar research work of Singh and Singh (2011), both treated and untreated rice husk ash and fly ash were characterized with the purpose of determining their mineralogical reinforcement properties in the metal matrix composites. The presence of hard phase materials in rice husk ash and fly ash suggesting them as green reinforcement materials in the metal matrix composites for the wear resistant applications. Also, Saravanan (2013) prepared AlSi10Mg composites reinforced with 3%–9% rice husk ash with different particle sizes of 50–75, 75–100 and 100–150 μm through the liquid metallurgy and the results revealed that the wear rate of the composite decreased with increasing weight percentage of rice husk. The composite samples reinforced with coarse rice husk particles exhibited better wear resistance in comparison to fine particles. Asafa (2015) fabricated aluminum metal matrix composites reinforced with snail shell particles with weight fraction of 16–48 wt% and size of 200–600 μm by stir casting technique. The results showed that aluminum composite with 48 wt% snail shell particles and size of 600 μm exhibited a tensile strength of 236 MPa and hardness of 48.3 HRF. Omole *et al.* (2014) manufactured green aluminum composites reinforced with

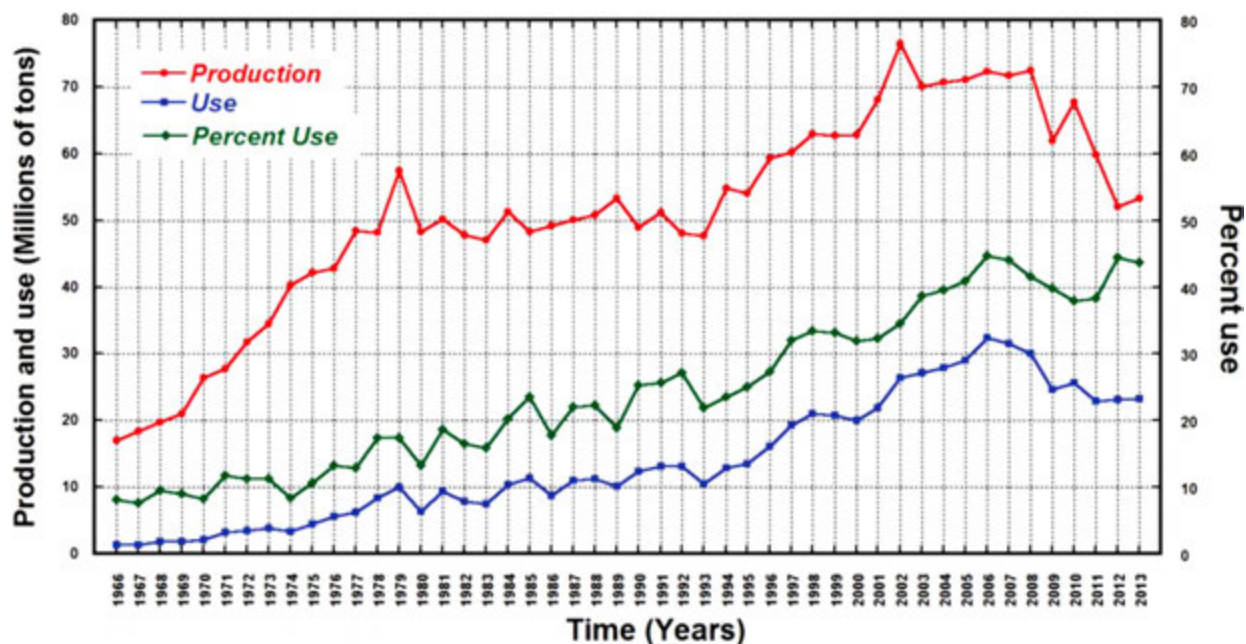


Fig. 4 Production, use, and use percentage of coal fly ash in the United States from 1966 to 2013. Reproduced from Bahrami, A., Soltani, N., Pech-Canul, M.I., Gutiérrez, C.A., 2016. Development of metal-matrix composites from industrial/agricultural waste materials and their derivatives. *Critical Reviews in Environmental Science and Technology* 46 (2), 143–208.

3–7 wt% walnut powder with mean grain size of 150 μm through stir casting and revealed that aluminum composite with 7 wt% of walnut powder exhibited the high hardness and tensile properties in comparison to other composites. A bibliographic review is presented below where aspects of suitability for the candidate elements in terms of mechanical and physical properties are analyzed. Green reinforcements for metal matrix composites are presented accordingly in order to identify which hold both adequate strength and stiffness performance along with affordable cost so as to be a promising proposal for a green composite to be applied in the near future on automotive and aerospace body panels.

Microstructure and Mechanical Properties of Green Aluminum Matrix Composites Reinforced with Fly Ash

Fly ash is one of the most inexpensive and low density reinforcement available in large quantities as solid waste by-product from combustion of coal in furnaces and thermal power plants. As it is known that fly ash particles are dangerous to breathe, the dust after it has settled on clothing, furniture, hands, etc. Further, fly-ash particles disposal is very costly. Fig. 4 shows significant growth in the production and consumption of coal fly ash since 1966 up to 2012 in the United States of America. Before the year 2008, a remarkable increase in the production and use of fly ash was observed for a period of about 15 years. Due to a general economic status, a decrease in coal use and to regulatory uncertainties, after 2008 a notable decrease was observed in the production and use during the five sequent years. However, a similar behavior was observed in the case of percent use but only for a couple of years, after which a recovery was noted, making it promising for several applications.

So by utilizing fly-ash particles as reinforcement material, some environmental problems which are occurring due to this ash can be removed. Fly ash particles are basically classified into two categories. One is cenosphere (hollow particle) and another one is precipitator (solid particle). Densities of fly ash particles including hollow and solid particles vary from 0.9 to 2.55 g cm^{-3} . The mechanical and physical properties of aluminum such as strength, hardness, wear resistance, stiffness, and reduction in density can be improved significantly by using the fly-ash as a reinforcement material. SEM micrographs of pure aluminum and aluminum-fly ash green composite are shown in Fig. 5. As can be seen from Fig. 5, the distribution of ash particles is not uniform due to the agglomeration of particles which clearly can be observed in the magnified micrograph shown in Fig. 5(c).

By adding 8 wt% of fly-ash particles in aluminum, the maximum tensile strength and hardness can be obtained (see Fig. 6). According to Table 1, ultimate strength increased from 52.23 MPa at 0 wt% to 139.79 MPa at 8 wt% and hardness increased from 34.5 to 48.5 HV, respectively. The increment in strength and hardness is due to the uniform distribution of ash particles in the aluminum matrix. As can be observed from Fig. 6 and Table 1, when fly-ash was mixed in aluminum beyond 8 wt%, hardness and strength of metal matrix composite began to decrease. This may be due to poor allocation and agglomeration of the ash particles in the aluminum matrix. The density of pure aluminum decreases with addition of fly ash particles into the aluminum matrix. The density of pure aluminum decreases from 2.71 to 2.53 g cm^{-3} at 8 wt% fly-ash reinforced aluminum composite.

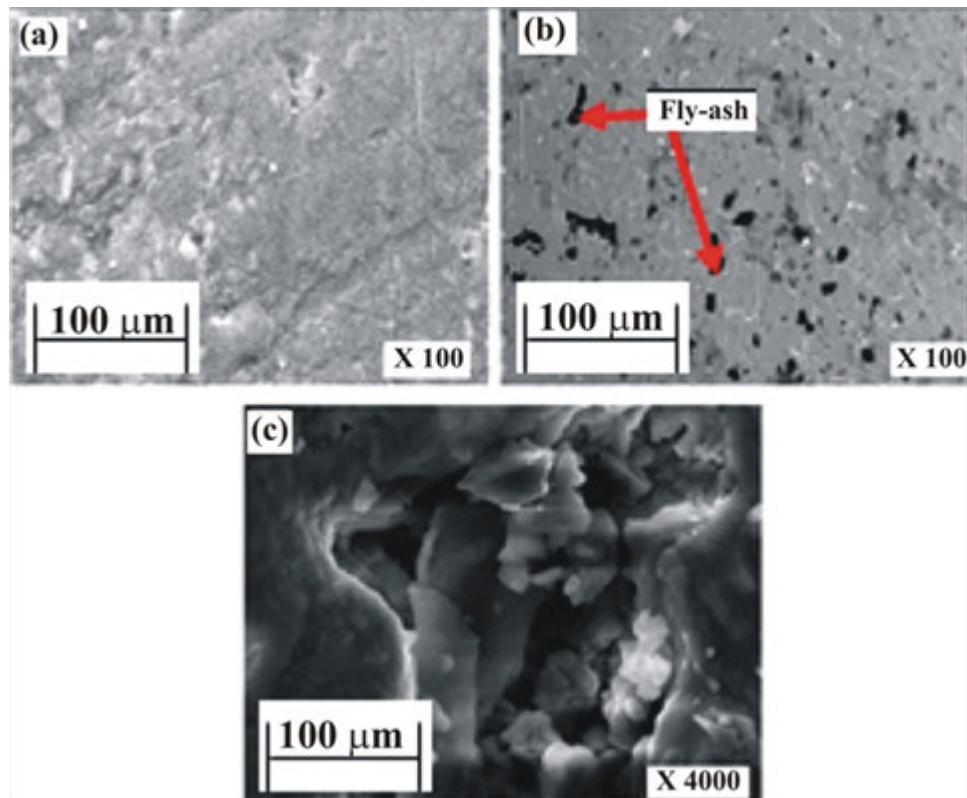


Fig. 5 SEM micrograph of (a) pure Al, (b and c) Al-8 wt% fly ash composite. Reproduced from Sharma, P.K., Dwivedi, S.P., Kumar, A., Sharma, A.K., 2019. Effect of magnesium addition on mechanical properties of Al-fly ash green composite produced under green ultrasonic vibration process. *International Journal of Precision Engineering and Manufacturing-Green Technology*, 1–8.

Potentials of Snail Shells as Reinforcement Material for Production of Green Aluminum Matrix Composites

Snail shells (see [Fig. 7](#)) which represent the discarded bio-shell waste of snails' pieces from restaurants create a serious degree of environmental warning with little economic value. The utilization of this waste as a low cost reinforcement material in the production of green metal matrix composite can find applications in automotive components like pistons, cylinder liners, and connecting rods as well as applications where lightweight materials are required with good stiffness and strength.

However, studies on the application of snail shells in the metal matrix composite have been rarely reported ([Bose et al., 2019](#); [Kolawole et al., 2017](#)). [Kolawole et al. \(2017\)](#) have investigated the physical properties of snail shell as a low cost reinforcement material in the metal matrix composites by means of a density determination, thermo-gravimetric analysis (TGA), refractoriness, energy dispersive X-ray (SEM/EDX), X-ray fluorescent (XRF), and the X-ray diffraction (XRD) analysis at 800°C, 850°C, and 900°C temperatures for 3 h. They reported that ([Kolawole et al., 2017](#)) snail shell powder possesses hard phase oxides (CaO, Fe₂O₃, Al₂O₃, Cr₂O₃, SiO₂, MnO, and NiO) at all studied temperatures and high thermal stability up to 670°C (see [Fig. 8](#)). The density of the snail shell powder was found to be 1.63 g cm⁻³ ([Kolawole et al., 2017](#)). This indicates that the snail shell powders are very light material and can reduce the overall weight of MMCs. The density value of snail shell powders are below the density value of fly ash, bagasse, bread fruit hull ash, coconut shell ash and silica, which are within the range 1.8 and 2.2 g cm⁻³. This result suggests that the snail shell powder looks promising as a reinforcing material in the production of light weight metal matrix composites at low costs when compared with the weight of agro or industrial wastes reinforcement material (fly ash, coconut shell ash, maize husk, and bagasse) in the production of green metal matrix composite. Also, the high thermal stability of the snail shell particles suggested it as a suitable candidate reinforcement material in the production of thermal resistance green metal matrix composites applicable in automotive components such as pistons and connecting rods.

The optical microstructure of un-alloyed aluminum and aluminum composite reinforced with 16 wt% of 600 μm size snail shell particles is shown in [Fig. 9](#). The microstructure of the unalloyed sample shows significant pores of varying sizes and shapes while that of aluminum composite reveals irregular snail shell particles distributed in aluminum matrix. In addition, the particles are uniformly distributed. The uniform distribution of snail shell particles in the matrix indicates the good wettability of the snail shell particles by the molten metal and good interfacial bonding between particles and matrix material. The tensile strength and hardness of pure aluminum (92.4 MPa, 29.2 HRF) are significantly enhanced by addition of 48 wt% snail shell particles with

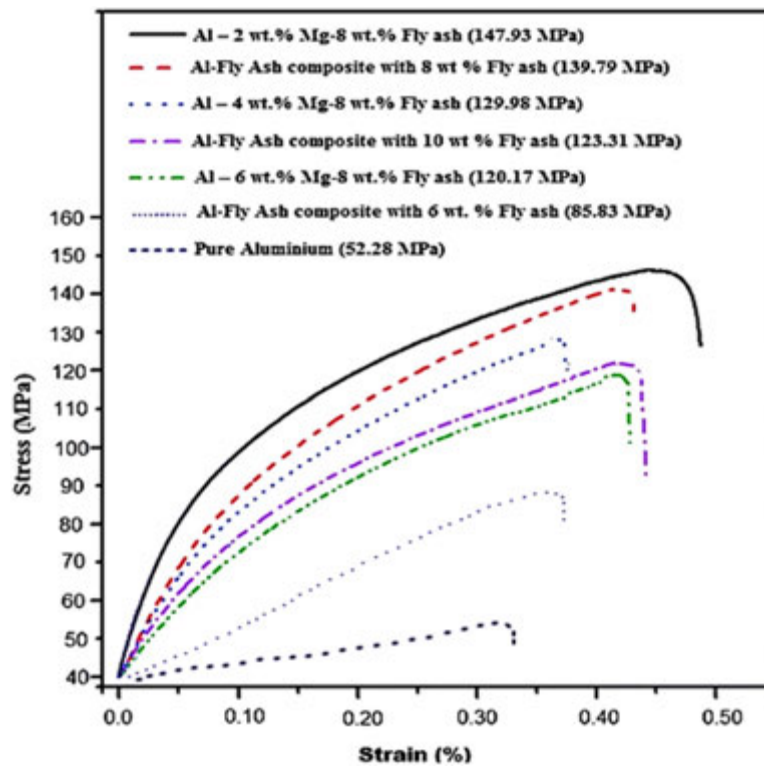


Fig. 6 Stress-strain diagram of various Al-Fly ash composites. Reproduced from Sharma, P.K., Dwivedi, S.P., Kumar, A., Sharma, A.K., 2019. Effect of magnesium addition on mechanical properties of Al-fly ash green composite produced under green ultrasonic vibration process. International Journal of Precision Engineering and Manufacturing-Green Technology, 1–8.

Table 1 Comparison of mechanical and physical properties of pure Al and Al-fly ash composites

Mechanical and physical properties	Pure Al	Al- 6 wt% fly ash composite	Al-8 wt% fly ash composite	Al-10 wt% fly ash composite
Density (gm/cm ³)	2.710	2.58	2.532	2.48
Hardness (HV)	34.5	40	48.5	45.5
Ultimate strength (MPa)	52.28	85.83	139.79	123.31
Strain (%)	0.34	0.37	0.43	0.44
Toughness (J)	40	15	6	4.5

Note: Sharma, P.K., Dwivedi, S.P., Kumar, A., Sharma, A.K., 2019. Effect of magnesium addition on mechanical properties of Al-fly ash green composite produced under green ultrasonic vibration process International. Journal of Precision Engineering and Manufacturing-Green Technology, 1–8.



Fig. 7 Snail shells (a) solid form and (b) powdered form. Reproduced from Kolawole, M.Y., Aweda, A., Abdulkareem, S., 2017. Archachatina marginata bio-shells as reinforcement material in metal matrix composites. International Journal of Automotive & Mechanical Engineering 14 (1).

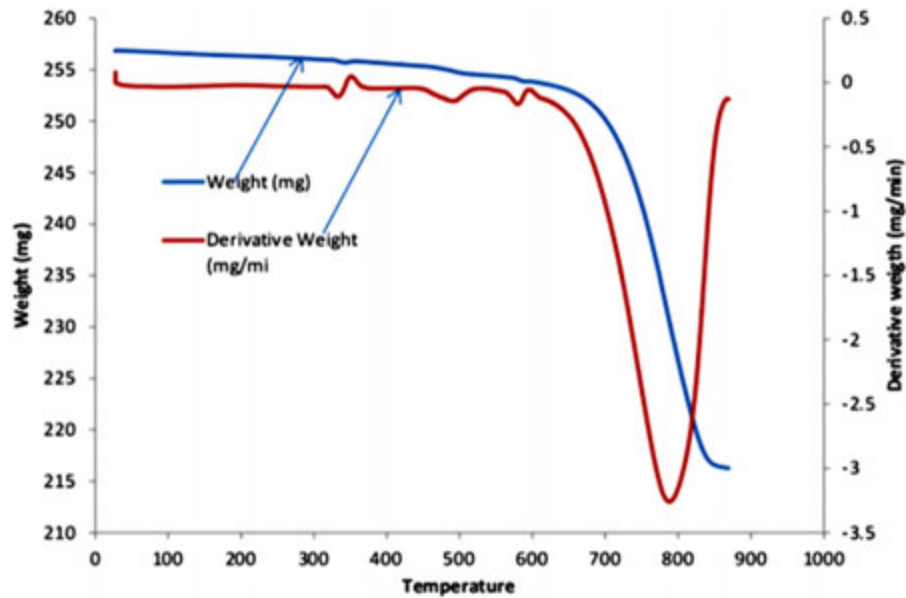


Fig. 8 Thermo-gravimetric analysis/differential thermal analysis curve for the snail shell powders. Reproduced from Kolawole, M.Y., Aweda, A., Abdulkareem, S., 2017. *Archachatina marginata* bio-shells as reinforcement material in metal matrix composites. *International Journal of Automotive & Mechanical Engineering* 14 (1).

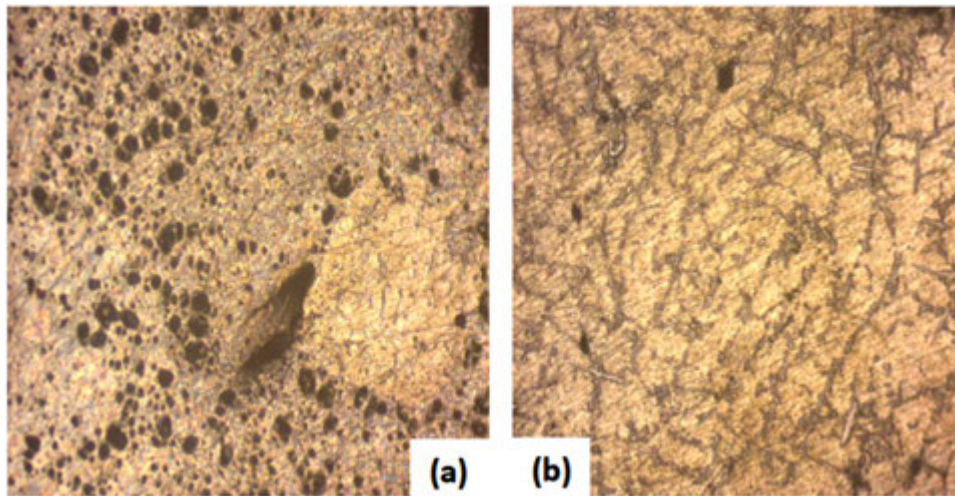


Fig. 9 Optical microstructure of (a) un-alloyed aluminum and (b) aluminum composite reinforced with 16 wt% of 600 μm size snail shell particles. Reproduced from Asafa, T.B., 2015. Potentials of snailshell as reinforcement for discarded aluminum based materials. *International Journal of Advanced Science and Technology* 84, 1–8.

particle size of 600 μm (236 MPa and 48.3 HRF, respectively). Therefore, snail shell particles can be used potentially as a low-cost reinforcement for engineering applications.

Production of Waste Eggshells-Reinforced Green Aluminum Matrix Composites

Chicken eggshell (ES) is an aviculture by-product that has been listed worldwide as one of the worst environmental problems, especially in those countries where the egg product industry is well developed. In the USA alone, about 150,000 tons of this material are disposed in landfills (Rath *et al.*, 2014). Chicken eggshell as a reinforcement material offers great opportunities because synthesized reinforcements can be produced in situ economically. Even though there have been several attempts to use chicken eggshell components for a variety of applications, its chemical composition and accessibility make chicken eggshell a probable source of biofiller-reinforced composites giving additional or improved thermal and mechanical properties. The other advantages of using chicken eggshell are its availability in bulk quantity with lightweight and being economical and environmental friendly. Although, chicken eggshells are the



Fig. 10 Photograph of: (a) Hen eggshells, (b) Dried eggshells, (c) Eggshells powder, and (d) Carbonized eggshells powder. Reproduced from Dwivedi, S.P., Sharma, S., Mishra, R.K., 2016. Mechanical and metallurgical characterizations of AA2014/eggshells waste particulate metal matrix composite. *International Journal of Precision Engineering and Manufacturing-Green Technology* 3 (3), 281–288.

waste products and very hazardous to our society they contain 95% CaCO_3 which can be directly used in the fabrication of metal matrix composite. **Fig. 10** shows the photograph of hen eggshell. Hen eggshells consist of ceramic materials. The chemical composition (by Weight) of by-product eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%), and organic matter (4%). To eliminate the covering layer of eggshell the hen eggshells often clean and dry under sun (as shown in **Fig. 8**). The dried eggshell ball milled to obtain eggshell powder then to remove the carbonaceous materials they carbonized at 500°C for 3 h. Dwivedi *et al.* (2017) have compared the mechanical and physical properties of AA2014/eggshells green metal matrix composite fabricated by electromagnetic stir casting technique with commercial reinforced metal matrix composite such as AA2014/ CaCO_3 particulate metal matrix composite and AA2014/SiC particulate metal matrix composite. **Fig. 11** shows the microstructures of AA2014 matrix composites reinforced with 12.5 wt% commercial CaCO_3 powder, 12.5 wt% un-carbonized eggshell powder, 12.5 wt% carbonized eggshell powder, and 10 wt% SiC particles, respectively. As can be seen from **Fig. 11**, the microstructure of AA2014/12.5 wt% carbonized eggshell particulate metal matrix composite presented a better result with respect to porosity than the other composites. Proper wettability was found at AA2014/SiC composite interface and AA2014/ carbonized eggshell composites interface, while no wettability can be observed at AA2014/ CaCO_3 composites interface (see **Fig. 12**). Hardness, tensile strength, and fatigue strength of AA2014 aluminum alloy can be improved by about 80%, 45.94%, and 53.33%, respectively, with the addition of 12.5 wt% carbonized eggshells particles, while toughness and ductility were reduced. Corrosion rate continuously decreases with the addition of eggshell particles in AA2014 aluminum alloy. The cost of metal matrix composite with 10 wt% SiC and 12.5 wt% eggshells' particulate were found to be about 13.33% higher and 12.5% lower, respectively, than that of AA2014 as shown in **Fig. 13**.

Also Hassan and Aigbodion (2015) found that the tensile strength of Al–Cu–Mg composites reinforced with egg shell particles increased by 8.16% at 12 wt% uncarbonized ES and 14.28% at 12 wt% carbonized ES, the hardness values increased by 10.01% at 12 wt% uncarbonized ES and 25.4% at 12 wt% carbonized ES with decrease in the density by 6.50% at 12 wt% uncarbonized ES and 7.4% at 12 wt% carbonized ES. The impact energy decreased by 23.5% at 12 wt% uncarbonized ES and 24.67% at 12 wt% carbonized ES particles, respectively.

Fabrication of Green Magnesium–Cenosphere Composites

Magnesium is a structural metal and getting more attention due to its capability of reducing the component weight by 354%, 155% and 55% if it replaces steel, titanium, and aluminum materials, respectively. Besides traditional engineering applications, magnesium is also biocompatible and forms an important part of bone. In addition, the use of magnesium-based materials has

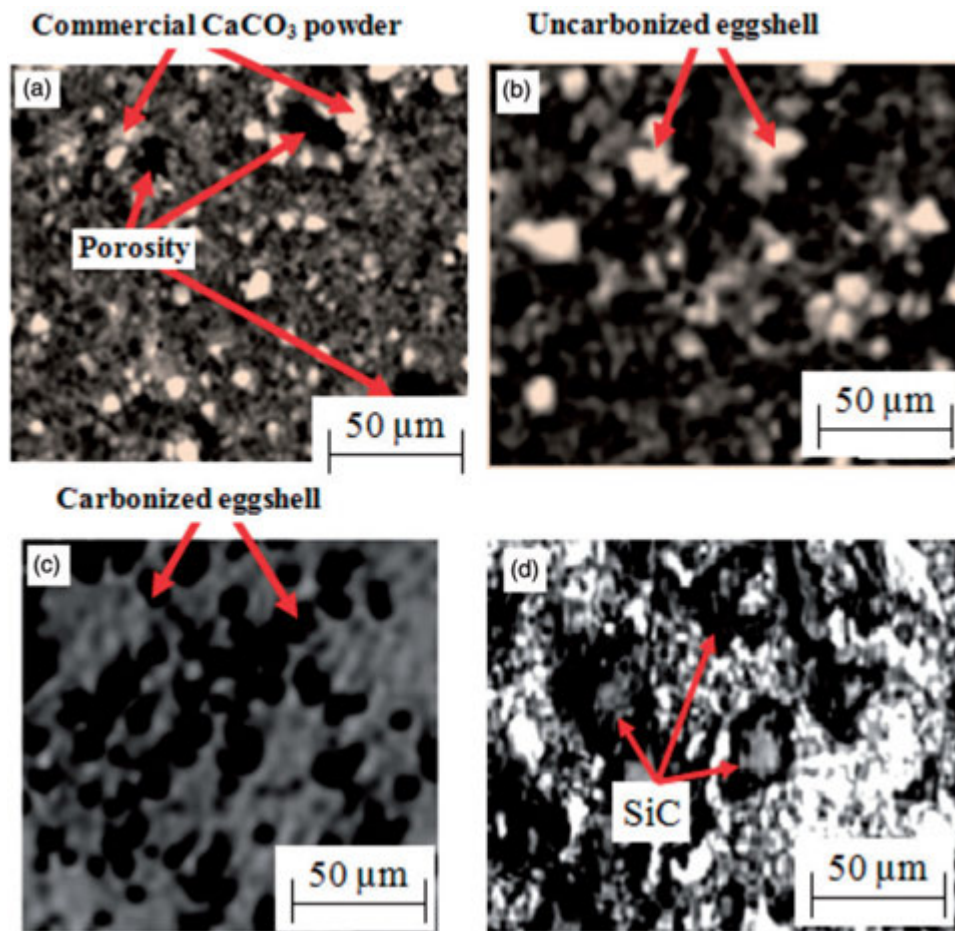


Fig. 11 Microstructure of aluminum composite reinforced with (a) 12.5 wt% commercial CaCO_3 powder, (b) 12.5 wt% uncarbonized eggshell powder, (c) 12.5 wt% carbonized eggshell powder, and (d) 10 wt% SiC particles. Reproduced from Dwivedi, S.P., Sharma, S., Mishra, R.K., 2017. A comparative study of waste eggshells, CaCO_3 , and SiC-reinforced AA2014 green metal matrix composites. *Journal of Composite Materials* 51 (17), 2407–2421.

the potential to maintain a sustainable ecosystem on earth. The mechanical properties, thermal properties, creep properties, and damping properties as well as corrosion resistance of magnesium materials have been significantly improved through alloying with other chemical elements or reinforcing with nano and/or micro particles. The weight of magnesium composites can further be reduced and approach that of plastics when magnesium materials are reinforced with hollow sphere particles. One type of well-known hollow spherical particles is called fly ash cenosphere particles which are naturally formed during the thermochemical process of coal-fired combustion in a coal-fired power plants. The cenosphere particle consists of mainly SiO_2 and Al_2O_3 and has very low density ($0.4\text{--}0.8\text{ g cc}^{-1}$) (Cay *et al.*, 2013; Rohatgi *et al.*, 2006). They are also strong, very cheap and widely available which make them attractive for many engineering applications. Alumina exhibits very good bonding with magnesium matrix and improves overall mechanical properties of magnesium. The integration of cenosphere particles into pure magnesium would create strong structural composite foams. Fig. 14 illustrates the morphology and distribution of cenosphere and secondary phase particles of the composite foams as well as presence of some micro-voids at the particles/magnesium matrix interface. As shown in Fig. 15, the cenosphere particles are fairly distributed in magnesium matrix and the amount of secondary phases was found to increase with the increasing amount of reinforcement.

Analyzing of the surface chemical elements using EDS and X-ray diffraction (XRD) show that the following chemical reactions led to the presence of MgO and Mg_2Si (Nguyen *et al.*, 2016):



Table 2 presents the thermal expansion coefficient and room temperature tensile properties of pure magnesium and its composite foam. According to Table 2, the thermal expansion coefficient of magnesium–cenosphere composite was significantly reduced due to the increasing presence of cenosphere particles. This indicates that magnesium–cenosphere composite are more dimensionally stable with respect to temperature. A remarkable increase in both yield strength and ultimate tensile strength can be

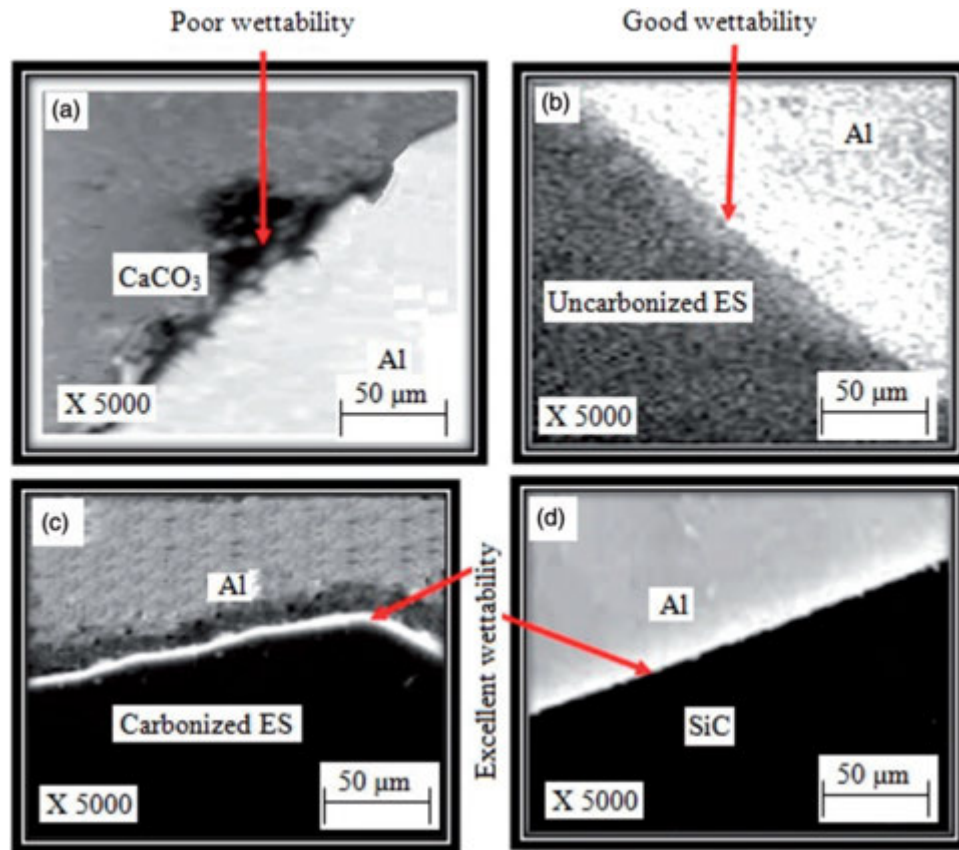


Fig. 12 Interfacial reaction layer of aluminum composite reinforced with (a) commercial CaCO_3 powder, (b) uncarbonized eggshell powder, (c) carbonized eggshell powder, and (d) SiC powder. Reproduced from Dwivedi, S.P., Sharma, S., Mishra, R.K., 2017. A comparative study of waste eggshells, CaCO_3 , and SiC-reinforced AA2014 green metal matrix composites. *Journal of Composite Materials* 51 (17), 2407–2421.

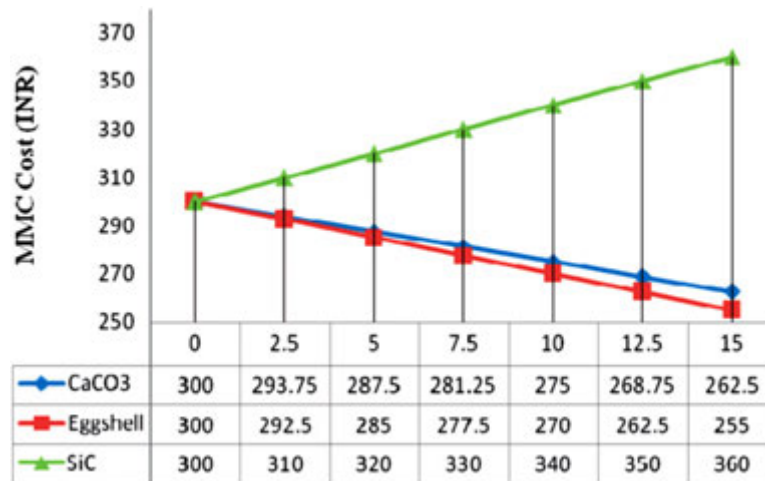


Fig. 13 Cost estimation of aluminum metal matrix composites. Reproduced from Dwivedi, S.P., Sharma, S., Mishra, R.K., 2017. A comparative study of waste eggshells, CaCO_3 , and SiC-reinforced AA2014 green metal matrix composites. *Journal of Composite Materials* 51 (17), 2407–2421.

obtained when cenosphere particles were added into magnesium due to the presence of reasonably well distributed harder cenosphere particles and the formation of hard secondary phases. A further increase in the amount of reinforcement beyond 5 wt% led to a gradual reduction in yield and ultimate tensile strengths of the composite foams; however, they remained higher than those of pure magnesium. One of the reasons for this reduction is much more micro-void formation at the uneven surface of hollow particles ($\sim 0.015\%$) and the formation of clusters. The tensile fracture surfaces of magnesium and composite foam

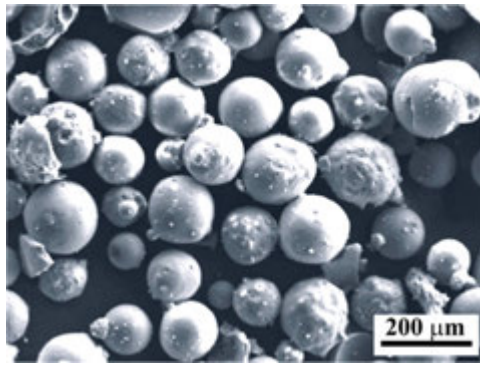


Fig. 14 Morphology of cenosphere particles. Reproduced from Nguyen, Q.B., Sharon Nai, M.L., Nguyen, A.S., *et al.*, 2016. Synthesis and properties of light weight magnesium–cenosphere composite. *Materials Science and Technology* 32 (9), 923–929.

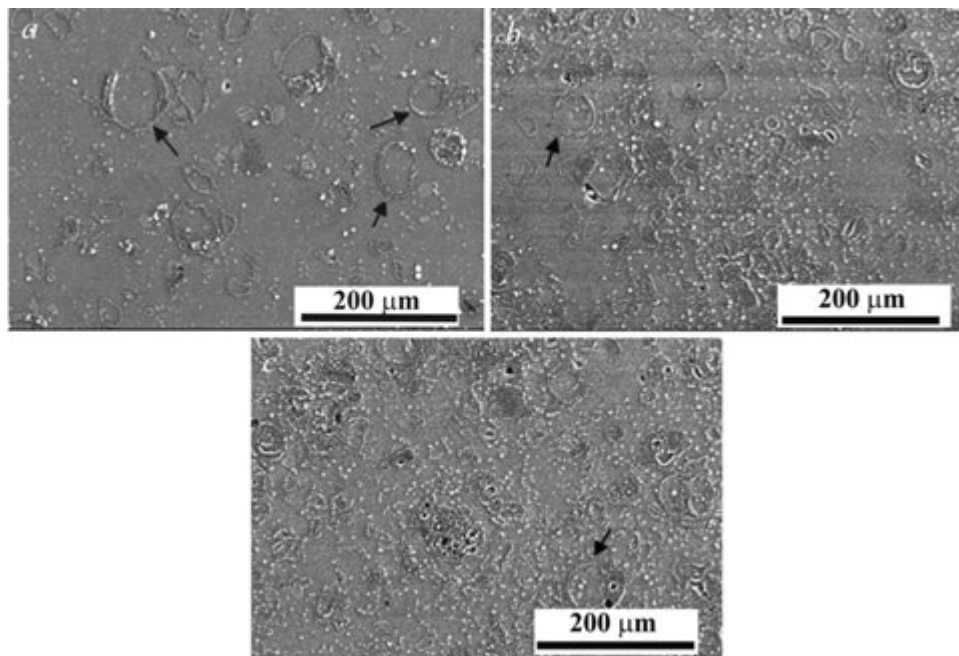


Fig. 15 Morphology and distribution of cenosphere particles in magnesium matrix with different amount of cenosphere addition: (a) 5, (b) 10, and (c) 15 wt%. Reproduced from Nguyen, Q.B., Sharon Nai, M.L., Nguyen, A.S., *et al.*, 2016. Synthesis and properties of light weight magnesium–cenosphere composite. *Materials Science and Technology* 32 (9), 923–929.

Table 2 Physical and mechanical properties of magnesium and magnesium–cenosphere composites

Material	Density ($g\ cc^{-1}$)		CTE ($10^{-6}\ K^{-1}$)	0.2YS (MPa)	UTS (MPa)	Tensile elongation (%)
	Theoretical	Experimental				
Mg	1.738	1.7361 ± 0.0004	27.1 ± 0.4	115 ± 5	170 ± 8	6.5 ± 1.1
Mg–5Ceno	1.5204	1.6406 ± 0.0048 (6%)	24.5 ± 0.5	180 ± 7	230 ± 10	5.1 ± 0.9
Mg–10Ceno	1.3512	1.4905 ± 0.0085 (17%)	22.5 ± 0.4	150 ± 8	215 ± 9	3.1 ± 1.0
Mg–15Ceno	1.2160	1.4203 ± 0.0136 (23%)	20.8 ± 0.6	130 ± 7	180 ± 8	1.5 ± 0.9

Note: Nguyen, Q.B., Sharon Nai, M.L., Nguyen, A.S., *et al.*, 2016. Synthesis and properties of light weight magnesium–cenosphere composite. *Materials Science and Technology* 32 (9), 923–929.

samples are shown in **Fig. 16**. The fracture surface of pure magnesium showed mixed mode fracture with the presence of microcracks and wavy lines indicating plastic deformation. However, fracture surface of magnesium–cenosphere composite showed significant presence of microcracks at the particle/matrix interface and broken or pull-off cenosphere particulates with limited plastic deformability.

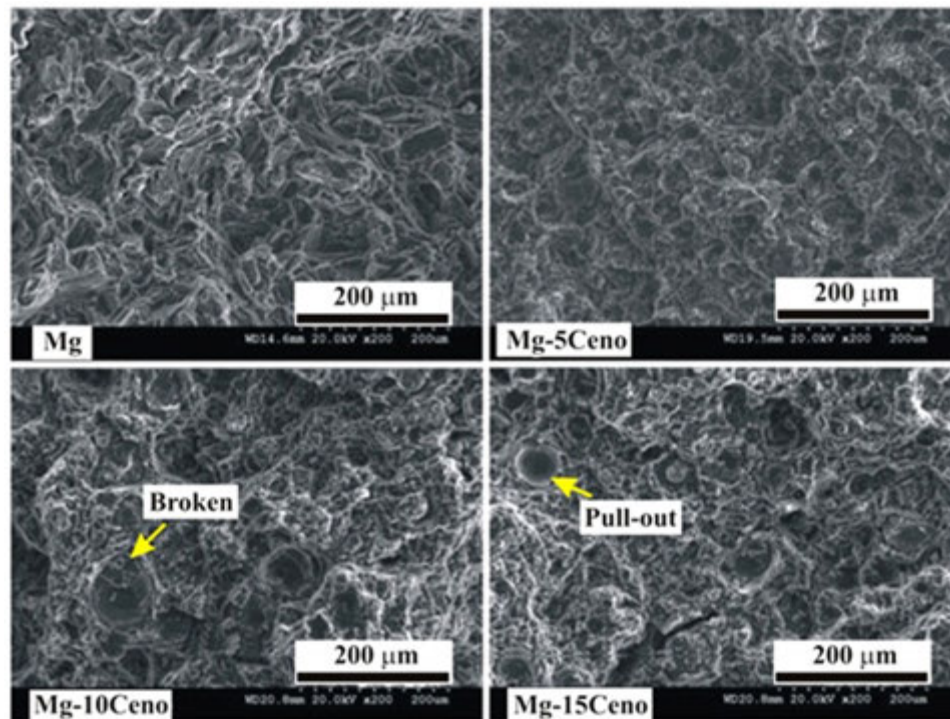


Fig. 16 Tensile fractographs of magnesium and magnesium-cenosphere composite. Reproduced from Rohatgi, P.K., Kim, J.K., Gupta, N., Alaraj, S., Daoud, A., 2006. Compressive characteristics of A356/fly ash cenosphere composites synthesized by pressure infiltration technique. *Composites Part A: Applied Science and Manufacturing* 37 (3), 430–437.

Conclusions

In this article, insight and information which is presented to be useful for future investigations on the development of green metal matrix composites using industrial and agricultural waste materials. On account of their attraction such as chemical composition, unlimited availability, and low-cost, industrial and agricultural waste materials comprise reasonable alternatives to replace reinforcing materials in metal matrix composites. Most of the industrial- and argo-waste materials contain valuable oxides, such as Al_2O_3 , SiO_2 , and Fe_2O_3 , which can act as reinforcing materials in their original composition or by a modification by means of suitable heat treatments.

Likewise, the investigations aimed at controlling the chemical composition of ceramic phases obtained from industrial or agricultural waste materials, the physical and mechanical properties of the resultant composites, are limited and constitute another window of opportunity. Due to lack of information of the real potential of industrial and agricultural wastes, their application in the development and fabrication of green metal matrix composites has been neglected. In order to facilitate their application toward new and innovative areas of economic interest and exploit their full potential as valuable resources, industrial and agricultural wastes must be the subject of strong and systematic studies. With the exception of the recent utilization of fly ash for the automotive industry, virtually no other waste material has been reused for a specific industrial application. In this context, an essential goal of this article is to excite the interest of academicians, scientists, technologists, and industrialists in the use of these materials for the fabrication of metal matrix composites. In the case of agricultural materials, a twofold perspective may apply, because while on the one hand, certain chemical elements have to be removed for specific applications, on the other hand, recovery of certain elements might be more attractive. Based on the significant progress observed so far, in terms of scientific and technological research, a promising future can be expected for the increased commercial production and usage of green based reinforcements in metal matrix composites. The proper use of industrial and agricultural waste materials requires knowledge generation for their usage in MMC preparation and for the industrialization stages.

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Surface Composites by Friction Stir Processing

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Nomenclature

DFSP Direct friction stir processing
FEA Finite element analysis
FSP Friction stir processing
HAZ Heat affected zone

MMCs Metal matrix composites
MWCNT Multi walled carbon nanotubes
NZ Nugget zone
TMAZ Thermo-mechanically affected zone

Glossary

Dynamic recrystallization Development of new grains and grain boundaries during plastic deformation.

Grain growth Development of large grains from fine grains.

Heat affected zone (HAZ) Regions next to thermo-mechanical affected zone subjected to severe heating resulted in FSP.

Intermetallics Compounds which are formed due to chemical reactions between elements.

Nugget zone (NZ) Center of the stir zone in FSP where material is subjected to intense plastic deformation and results in grain refinement.

Recrystallization Development of completely new grains and grain boundaries in metals and alloys at a specific temperature.

Thermo-mechanically affected zone (TMAZ) Interface region produced in FSP adjacent to nugget zone.

Introduction

Surface composites are a class of modern engineered materials in which reinforcements are introduced at the surface up to a certain depth without affecting the chemical composition of the core of the structure. In some industrial applications, altering the surface properties is crucial to enhance the life span and the performance of the structure. Chemical composition and microstructure at the surface influence a few crucial properties, particularly structure sensitive properties such as mass loss due to wear and degradation due to corrosion. When the surface is incorporated with reinforcements without affecting the microstructure and chemical composition of the core of the structure, surface alone exhibits higher hardness and wear resistance and the material in bulk experiences negligible loss to its toughness. Centrifugal casting, laser melt treatment, and plasma spraying are a few examples for liquid state methods to develop surface composites (Ayers and Tucker, 1980; Weisheit *et al.*, 2014; Nikhilesh and Krishan, 2014). In liquid state methods, handling the liquid metal is a complex issue. Furthermore, oxidation of liquid metal and formation of intermetallics, development of coarse grains during solidification, agglomeration of the reinforced particles are the important issues must be paid attention to successfully produce surface composites. On the other hand, solid state routes such as powder metallurgy, diffusion bonding, friction surfacing, and friction stir processing offer several advantages and address the issues that are associated with liquid state methods (Davis and Ward, 1993; Mishra and Ma, 2014). In solid state routes, solid–solid diffusion mechanism and dynamic recrystallization play important roles in developing surface composites. Among the available solid state routes, friction stir processing has emerged as a promising alternate method to develop surface composites within the solid state.

Development of Surface Composites by FSP

The invention of friction stir welding in the year of 1991 at The Welding Institute, UK has opened a new field of manufacturing engineering and led to develop several other derivative processes such as friction stir processing, friction surfacing, friction stir spot welding, friction free form, etc. Generating heat from friction is the one fundamental and common observation that can be made in all these friction based processes in addition to eliminating the liquid state during processing. Among all these solid state processes, friction stir processing (FSP) has been widely investigated to modify the surface microstructure of metallic plates and sheets. In FSP, a non-consumable rotating tool is plunged into a plate or sheet and traverse motion is given while a suitable load is continually applied (Mishra and Ma, 2014). Workpiece remains in the solid state and formation of intermetallics and oxidation can be minimized to a great extent. During the intense plastic deformation, very fine grains are produced within the stir zone due to dynamic recrystallization (Mishra *et al.*, 2000). This facilitates to achieve improved properties which are structure sensitive in the processed region. Developing surface composites by FSP is a novel route initially demonstrated by Mishra and Ma (2014). The principle of developing surface composite is simple as schematically explained in Fig. 1. Before FSP, grooves or holes are

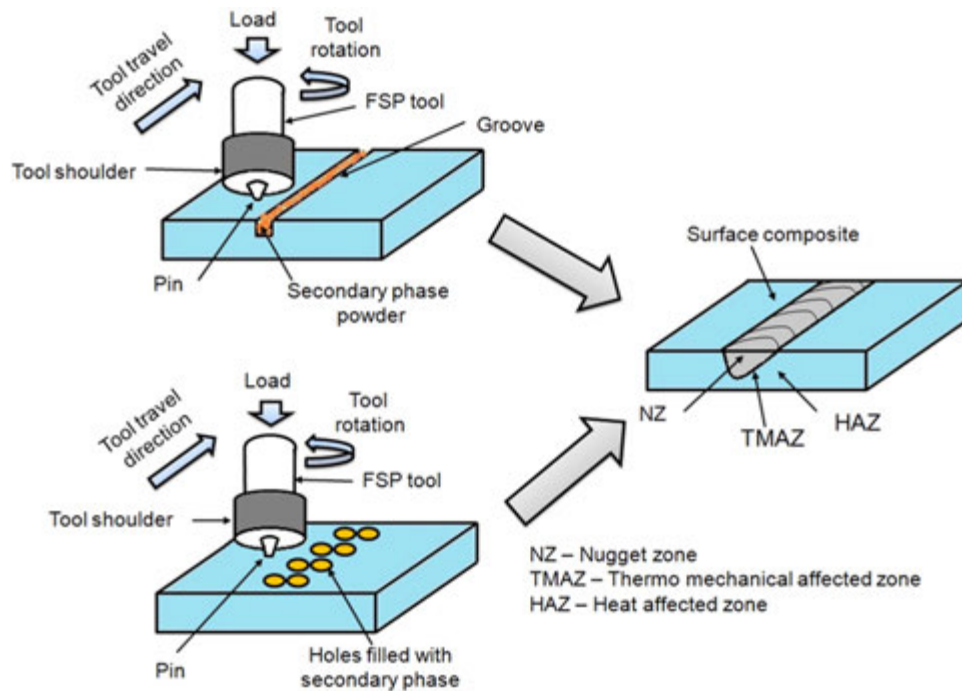


Fig. 1 Schematic representation of composite fabrication by FSP. Modified from Ratna Sunil, B., 2016. Different strategies of secondary phase incorporation into metallic sheets by friction stir processing in developing surface composites. *International Journal of Mechanical and Materials Engineering* 11, 12. doi:10.1186/s40712-016-0066-y.

produced on the surface of the plate or sheet and filled with the reinforcing particles (Ratna Sunil, 2016; Saikrishna *et al.*, 2016). Then, FSP is carried out by using a non-consumable tool to embed the reinforcements into the surface. After FSP at the cross section, three distinct regions known as nugget zone (NZ), thermo-mechanically affected zone (TMAZ) and heat affected zone (HAZ) can be seen as schematically illustrated in Fig. 1 which exhibit different microstructural features. These regions are mostly limited beneath the shoulder of the FSP tool and adjacent to the stir zone. The level of particles distribution into the surface depends on the process parameters such as tool rotational speed, travel speed, penetration depth, tool tilt angle, and pre-heating of the workpiece. In addition to composite formation, smaller grains are also resulted in the stir zone due to dynamic recrystallization which further help to improve the properties of the surface composite.

When the FSP tool rotates and stirs the material at the surface of a workpiece, secondary phase particles are distributed along the material flow across the stir zone. The width of the stir zone depends on the dimensions of the FSP tool shoulder. Several factors affect the level of particle distribution in FSP. Tool geometry is one among the other influencing factors, which must be paid keen attention. Designing FSP tool with appropriate geometry is the first step that dictates the success of the process. Tool geometry includes diameter of the shoulder, dimensions of the pin, profile of the pin, and shoulder diameter to pin diameter ratio.

Methods of Secondary Phase Introduction into the Matrix by FSP

Incorporating the secondary phase into the surface of the workpiece without melting the substrate is challenging. Intended reinforcement is needed to be available at the surface to readily mix along with the material that is stirred and flowed around the tool pin during FSP. The level of distribution of the dispersing phase depends on the kind of method used to incorporate the reinforcing particles. Along with the other influencing factors such as tool design and processing parameters, method of secondary phase incorporation is also found to have a major role particularly on distributing the powder particles to produce a successful composite (Gandra *et al.*, 2011; Miranda *et al.*, 2013). The thickness of the composite layer produced using FSP also depends on the method of secondary phase incorporation.

Groove filling method was the first route introduced by Mishra *et al.* (2003) to develop 7075-SiC composite by FSP. In this method, a narrow groove is produced on the surface of the sheet or plate is completely filled with the reinforcement. Then, FSP is carried out to stir the material at the surface to produce the surface MMCs as schematically shown in Fig. 1 (Ratna Sunil *et al.*, 2014; Mishra *et al.*, 2003). Later on, pre-surfacing process by using a non consumable pin-less tool was proposed to avoid the escape of the reinforcement from the groove before doing actual FSP (Lee *et al.*, 2006). This modified method helps to arrest the secondary phase particle within the groove and the particles do not to fly away or escape from the groove during FSP. Fig. 2(a) shows typical photograph of workpiece with grooves and Fig. 2(b) shows developing surface composite of AZ31 Mg alloy-hydroxyapatite by FSP (Ratna Sunil, 2016). In order to prevent the escape of the filled particles from the grooves/holes during FSP, pre-surface treatment by

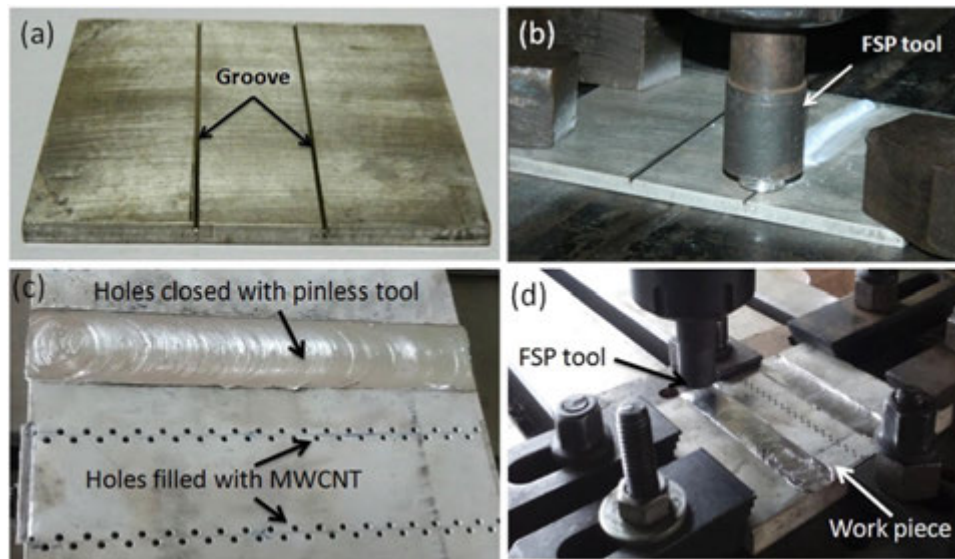


Fig. 2 Photographs of workpieces and FSP process: (a) grooves on AZ31 Mg alloy sheet, (b) developing AZ31–hydroxyapatite composite by FSP, (c) holes filled with multi walled carbon nanotubes (MWCNT) and subjected to surfacing by pin-less tool, and (d) developing composite of Mg–MWCNT by FSP. (a) and (b) Reproduced with permission from Ratna Sunil, B., Sampath Kumar, T.S., Chakkingal, U., Nandakumar, V., Doble, M., 2014. Nano-hydroxyapatite reinforced AZ31 magnesium alloy by friction stir processing: A solid state processing for biodegradable metal matrix composites. *Journal of Materials Science: Materials in Medicine* 25, 975–988.

using a pin-less FSP tool also can be adopted to close the groove. **Fig. 2(c)** shows a photograph of holes filled with CNT on pure Mg sheet. **Fig. 2(d)** shows incorporating CNTs into Mg workpiece by using pin-less FSP tool followed by processing with designed FSP tool (Saikrishna *et al.*, 2016). Holes filling method is another widely used route to incorporate secondary phase into the surface of the workpiece in developing surface composites by FSP. Initially, tiny holes are produced on the surface of the workpiece and the secondary phase particles are filled in the holes before FSP (Yang *et al.*, 2010; Akramifard *et al.*, 2014). Then, the actual FSP is carried out similar to groove filling method. Additionally, holes filling and closing method, similar to grooves filling method, has also been employed to eliminate the escape of the reinforcement (Madhusudhan Reddy *et al.*, 2013).

Mertens *et al.* (2012) illustrated another method of secondary phase introduction into the matrix by FSP known as sandwich method as schematically illustrated in **Fig. 3(a)**. In this method, secondary phase is arranged in the form of a layers or laminas between the base sheets or plates of matrix material. Then, FSP is done such a way that the FSP tool pin is penetrated through the plates and the secondary phase layer or lamina. Due to the stirring action and traverse motion of the FSP tool, the secondary phase layer or lamina is broken into small particles or fibers, and distributed into the matrix phase and results a composite.

Providing the surface coatings followed by FSP is another strategy to incorporate the secondary phases into the matrix material (Mazaheri *et al.*, 2014; Kurt *et al.*, 2011). In this method, a surface coating of secondary phase is developed on the workpiece before FSP. Then, FSP is carried out on the surface as schematically shown in **Fig. 3(b)** to produce the surface composite. When the rotating FSP tool introduces plastic deformation, mixing of the coated surface and the matrix material results a composite layer. Huang *et al.* (2014) illustrated a new design in developing FSP tool which facilitates embedding reinforcement directly through a channel provided within the tool during FSP. This specially designed FSP tool as illustrated in **Fig. 3(c)** is provided a longitudinal channel within the tool through which reinforcement is incorporated into the surface. This new design has been named as direct friction stir processing (DFSP) tool. Several authors have reported using different strategies to incorporate reinforcement. The maximum thickness of the surface composite layer produced in each strategy has been briefly summarized and presented in **Table 1**. It can be understood that groove filling route is optimum to develop surface composites with higher thickness.

Heat Generation and Dissipation

In FSP, heat is generated within the workpiece which reduces the yield strength of the workpiece locally beneath the shoulder of the tool. Therefore, the material undergoes plastic deformation at lower amount of loads and material plastic flow around the stirring tool pin can be observed. The total heat that is produced in FSP usually raises the temperature of the processed zone up to ≈ 0.7 – 0.8 times of melting temperature of the base material. While developing surface composites by FSP, heat is generated due to the three reasons as given below:

- (1) Friction between the rotating FSP tool pin and the workpiece.
- (2) Friction between the tool shoulder and the workpiece surface.
- (3) Plastic deformation of the workpiece.

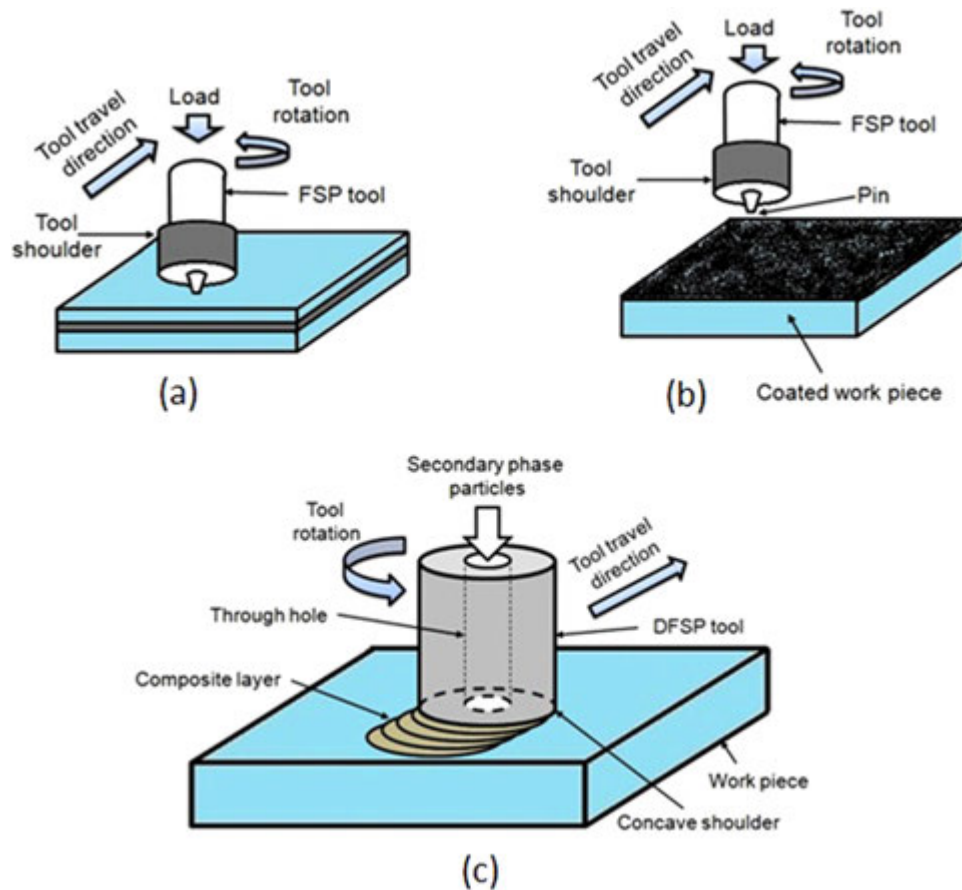


Fig. 3 Schematic representation of method of particle incorporation in FSP: (a) sandwich method, (b) surface coating method, and (c) direct FSP tool method. Modified from Ratna Sunil, B., 2016. Different strategies of secondary phase incorporation into metallic sheets by friction stir processing in developing surface composites. *International Journal of Mechanical and Materials Engineering* 11, 12. doi:10.1186/s40712-016-0066-y.

The generated heat in the stir zone is usually lower compared with the liquid state methods. However, the amount of produced heat is sufficient to introduce solid state plastic deformation. Conduction, convection and radiation are the mechanisms by which heat loss in FSP is happened. Heat transfer through Workpiece, anvil, FSP tool, and ambient environment are the four basic possibilities by which the produced heat is dissipated in FSP (Fig. 4). Major fraction of the heat produced in the stir zone is transfer through the workpiece and the tool. Later on, heat is transferred through the work table or the anvil that supports and holds the workpiece. During FSP, minor fraction of produced heat is escaped to the environment by conduction and radiation. The amount of heat transfer is lower in FSP compared with liquid state routes and hence decreases residual stresses in the produced composite. Additionally, solidification of the processed zone is not seen in FSP as it is a solid state process which also eliminates residual stresses and distortion resulted during the shrinkage of the liquid in the processed zone. The amount of heat generated and transferred during FSP influence the success of developing surface composites. Heat generation in the stir zone depends on several processing parameters including FSP tool rotational speed, tool travel speed, tool penetration depth, and applied load. For every material system, the process parameters must be optimized to develop surface composite without defects.

Material Flow Mechanisms

The material flow behavior during FSP while developing surface composites depends on several crucial factors as given below:

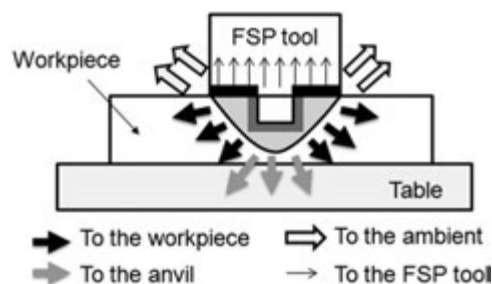
- (1) Process parameters including tool rotational speed, travel speed, penetration depth, and load.
- (2) Tool geometry including pin and shoulder dimensions, ratio of shoulder diameter to pin diameter, type of pin, and shoulder profiles.
- (3) Material characteristics and preheating of the material.

Different experimental techniques and computational methods have been used to understand the flow patterns of material during stirring beneath the FSP tool shoulder. Marker tracer technique and welding of dissimilar metals are the two important strategies reported in the literature to understand the material flow behavior during FSP. Furthermore, a few numerical methods

Table 1 Surface composites of different materials produced by FSP and the thickness of the composite layer from different methods of secondary phase incorporation

Material system	Secondary phase	Method of secondary phase incorporation	Composite layer thickness (mm)	Reference
Aluminum/its alloys	SiC	Groove filling	2	(Wang <i>et al.</i> , 2009)
	Al ₂ O ₃	Groove filling and closing	4	(Shafiei-Zarghani <i>et al.</i> , 2009)
	MWCNTs	Groove filling	2.2	(Lim <i>et al.</i> , 2009)
	Al ₂ O ₃	Holes filling	3	(Yang <i>et al.</i> , 2010)
	SiC and MoS ₂	Groove filling	3.5	(Alidokht <i>et al.</i> , 2011)
	Ni particles	Groove filling	0.15	(Devinder and Bauri, 2011)
	Al ₂ O ₃	Groove filling and closing	3.8	(Sharifitabar <i>et al.</i> , 2011)
	TiC B ₄ C	Groove filling	6	(Maxwell Rejil <i>et al.</i> , 2012)
	Graphite, Al ₂ O ₃ and SiC	Groove filling	3.5	(Anvari <i>et al.</i> , 2013)
	SiC and Al ₂ O ₃	Surface coating and FSP	0.204	(Miranda <i>et al.</i> , 2013)
Magnesium/its alloys	Al ₂ O ₃	Surface coating and FSP	0.1	(Mazaheri <i>et al.</i> , 2014)
	SiO ₂	Groove filling and closing	3–3.5	(Lee <i>et al.</i> , 2006)
	CNTs	Groove filling	2	(Morisada <i>et al.</i> , 2006)
	SiC	Groove filling and closing	2.5	(Asadi <i>et al.</i> , 2011)
	Al ₂ O ₃	Groove filling	5–6	(Azizieh <i>et al.</i> , 2011)
	Al ₂ O ₃	Groove filling	2–2.5	(Faraji <i>et al.</i> , 2011)
	Carbon fibers	Sandwich method	2.7	(Mertens <i>et al.</i> , 2012)
	SiC and B ₄ C	Holes filling and closing	3	(Madhusudhan Reddy <i>et al.</i> , 2013)
	SiC	Direct friction stir processing tool	0.15	(Huang <i>et al.</i> , 2014)
	Hydroxyapatite	Groove filling	2	(Ratna Sunil, 2016)
Copper/its alloys	SiC	Groove filling	2	(Barmouz <i>et al.</i> , 2011)
	Graphite	Groove filling and closing	Not reported	(Sarmadi <i>et al.</i> , 2013)
	B ₄ C	Groove filling and closing	5	(Sathiskumar <i>et al.</i> , 2013)
	TiC	Holes filling and closing	Not reported	(Sabbaghian <i>et al.</i> , 2014)
	SiC	Holes filling	Not reported	(Akramifard <i>et al.</i> , 2014)
Titanium/its alloys	Hydroxyapatite	(1) Groove filling (2) Surface coating	0.16	(Farnoush <i>et al.</i> , 2013b)
	Hydroxyapatite	Holes filling	0.16	(Farnoush <i>et al.</i> , 2013a)
Steels	TiC	(1) Groove filling (2) surface coating	1.5–2	(Ghasemi-Kahrizsangi and Kashani-Bozorg, 2012)

Source: Ratna Sunil, B., 2016. Different strategies of secondary phase incorporation into metallic sheets by friction stir processing in developing surface composites. International Journal of Mechanical and Materials Engineering 11, 12. doi:10.1186/s40712-016-0066-y.

**Fig. 4** Heat distribution from the processed zone after FSP.

such as finite element analysis (FEA) were also adopted to visualize the flow of material during FSP. Marker tracer technique involves introducing a material having different chemical properties compared with the base material into the surface of the base material followed by chemical etching to distinctly identify the flow of the dispersed material. Copper, aluminum, aluminum composite, steel, and tungsten wire are a few examples for the marker materials. Based on the results, the following observations can be made to understand the material flow during FSP:

- (1) The material flow is non-symmetric with reference to the center line of the stir zone.
- (2) The material flow in the backward direction is limited to a distance equal to the diameter of the FSP tool pin.
- (3) Both the advancing and retreating sides show a clear distinction and the material across the stir zone is not uniformly stirred.
- (4) The material flow direction is initially found to be in the downward direction at the advancing side and then in the upward direction at the retreating side. The rate of material flow is higher around the pin beneath the shoulder.
- (5) The rate of material flow in the vertical direction at the retreating side is inversely proportional to the rate of tool advancement per a rotation.
- (6) Increased material flow can be achieved across the center line of the stir zone by increasing the pin diameter at the same process parameters.

From the works of Reynolds (2000) and Seidel and Reynolds (2001) the material flow can be visualized as a localized extrusion of the stirred material around the pin. Colligan (Colligan, 1999a,b) demonstrated using small steel balls (0.38 mm diameter) as the dispersing material in an aluminum alloy matrix to understand the material flow during FSW. From the radiography studies after processing, the distribution of the steel shots was observed as broader at the top regions of welding. Furthermore, extrusion of the material through the threads of pin was also observed and suggested that the material in the weld zone may not completely undergo stirring but is extruded through the pin threads. London *et al.* (2003) used Al6061-30%SiC and Al-20%W composites as markers and the material flow was observed as happened in three steps when threaded pin profile is used. Initially, uplifting of the material is happened in front of the pin due to the tool tilt. Then, material shear is happened around the pin followed by downward movement of the material due to the threads on the pin. Additionally, the distribution of the marker was observed as higher at the advancing side compared with center of the stir zone. On the other hand, Midling (1994) demonstrated dissimilar metals welding to understand the material flow. Two dissimilar aluminum alloys were welded and the interface shapes from the microstructural studies were observed. From the works of Ouyang and Kovacevic (2002), mechanically mixed regions with vortex-like structure and alternative lamellae were observed in the weld joint 2024Al and 6061Al dissimilar alloys due to stirring action of the tool and the localized in situ extrusion. However, other material flow patterns were also reported by several authors. Among them, onion ring patterns are one typical observation in many alloy systems as reported by Krishnan (2002), Biallas *et al.* (1999), Mahoney *et al.* (1998) and Sutton *et al.* (2002).

Along with the experimental works, several numerical methods have been adopted to understand the mechanisms behind the material flow during FSP (Ma *et al.*, 2000a,b; Xu *et al.*, 2001; Dong *et al.*, 2001). From these results, the level of understanding of the material flow during FSP has been elevated. Based on the studies of Arbogast (2003), the material flow in FSP is considered as the combinations of different metal forming processes as given below and as schematically illustrated in Fig. 5:

- (1) Preheating
- (2) Initial deformation
- (3) Localized extrusion
- (4) Localized forging
- (5) Post heating and cooling

When the rotating FSP tool is plunged into the workpiece and moved across the grooves or holes, initially, the material is pre-heated due to the generated heat due to friction and plastic deformation of the material in the stir zone. The temperature that is observed in the pre-heating zone depends on process parameters and the tool geometry. As the FSP tool is advancing, the material beneath the shoulder is subjected to stirring when the stresses reach beyond the flow stress of the material. Then, the material starts deformation and moves toward the shoulder and into the localized extrusion zone where the material is extruded from the front of the pin to the rear of the pin. A swirl motion of the material can also be seen at the bottom of the pin limited to a small region.

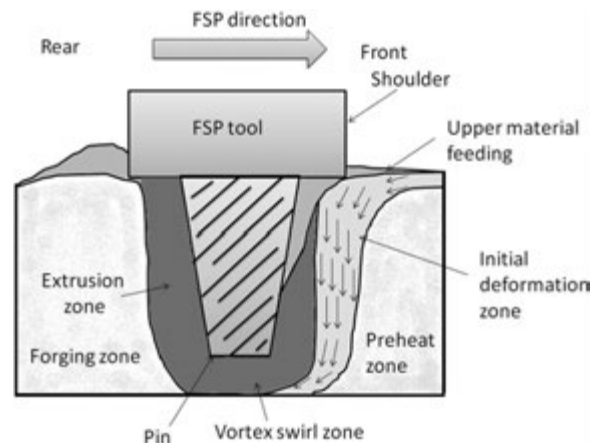


Fig. 5 Schematic illustration of material flow in different zones resulted during FSP.

Further, the extruded material is subjected to forging due to the load imposed by the rotating shoulder. When the FSP tool advances, the cavity produced by the pin is filled by the extruded material. The hydrostatic pressure that is imposed by the rotating tool shoulder encapsulates the stirring material within the processed zone. Then, the FSPed region is cooled down in the post heating/cooling zone. From the overall observations, the material flow behavior in FSP is complex as it involves several combinations of mechanisms at the microscopic level.

Material Properties Influenced by FSP

Developing composites by FSP involves altering two important factors (1) grain size and (2) chemical composition at the surface. Usually, FSP results in grain refinement in the stir zone. Additionally by externally adding secondary phase particles during FSP, material properties are significantly altered. Furthermore, phase distribution, formation of supersaturated grains, and preferred orientation are the other changes which are seen in FSPed materials. Surface composites produced by FSP usually exhibit improved material properties compared with that of composites produced by liquid processing routes. Elastic modulus, hardness, and tensile strength of the composite material are improved due to the altered chemical composition. Additionally, smaller grain size in the processed zone introduces grain boundary strengthening effect. Wear resistance of the surface composite is increased due to the incorporated hard phase particles into the surface along with the grain refinement. Fatigue is another crucial property which can be improved for a material by producing smaller grains and dispersing fine dispersing phases, i.e., nanosized particles by FSP. Thermal conductivity of the composite can be modified by using appropriate dispersing phase during FSP. Damping properties of a material can be changed by introducing a suitable reinforcement into the matrix by FSP. Corrosion behavior is another important material property that depends on several factors including grain size, amount and size of the dispersing phase, electrochemical behavior of the reinforcement, etc. The microstructural changes and altered surface composition after FSP alter the electrochemical events. The corrosion behavior of the surface composite depends on the matrix and the dispersing phase when they combined exposed to corroding medium. Therefore, FSP influences the corrosion behavior of the surface composite positively or negatively, but the changes are significant.

Defects in the Surface Composites Produced by FSP

Similar to any other manufacturing process, inappropriate processing parameters may produce defects in the surface composites produced by FSP. The material flow behavior in friction stir welding (FSW) and FSP is almost similar. The objective of FSW is to establish a metallurgical continuity between two surfaces (known as welding). The objective of FSP is to alter the microstructure at the surface of a material without melting the substrate. The working principle and the material flow are almost the same in FSW and FSP. Secondary phase particles are embedded into the matrix material while developing surface composites by FSP. Thermal conductivity and material flow rate during FSP in the stir zone are influenced by the incorporated reinforcements. However, the types of defects are similar to that of FSW but the level of defects formation is more. Common defects which can be seen in the surface composite produced by FSP include wormhole, lack of fusion, lack of penetration, scalloping, surface lack of fill, surfacing galling, root flow defect, and nugget collapse (Arbégast, 2003). Fig. 6 shows common defects observed in FSP as explained by Arbégast (2003). Excess amount of heat generation or insufficient amount of heat generation results combination of these defects in the composites developed by FSP.

If the generated heat in the stir zone is higher, severe material flow is observed that leads to formation of the flash, nugget collapse and surface galling defects. If the material flow is poor due to insufficient heat generation, defects like worm hole and lack of fill are resulted. The material flow rates and transfer rates are different at the advancing side and retreating side during FSP. Therefore, different levels of material flows give variations in the formation of defects intensity at the advancing side and at the retreating side (Nandan *et al.*, 2008). Among the other influencing factors, tool penetrating depth is one important parameter that also needs additional attention while adopting optimized process parameters. Sufficient tool penetration depth is given such that the tool shoulder touches the workpiece surface and generates sufficient heat due to friction to plastically stir the material beneath the shoulder with the help of tool pin. Excess penetration results formation of flash and insufficient penetration leaves a groove or open channel instead of introducing plastic flow of the material. Additionally, inappropriate penetration depth also forms tunneling defects and longitudinal cracks.

Effect of Process Parameters

Tool Design

Designing FSP tool with optimum geometry is crucial to successfully develop surface composites by FSP. The three important function of an FSP tool are (1) heating the workpiece, (2) causing material flow, and (3) encapsulating the plasticized material beneath the tool shoulder. Tool geometry dictates the success of composites development using FSP. Appropriate tool design gives better material flow and reduces or completely eliminates the defects in the produced composite. Tool shoulder influences the amount of heat generation and controls the material flow at the surface. Various surface profiles such as scroll, flat, ridges, knurling, and groves are provided to the shoulder to control the material flow.

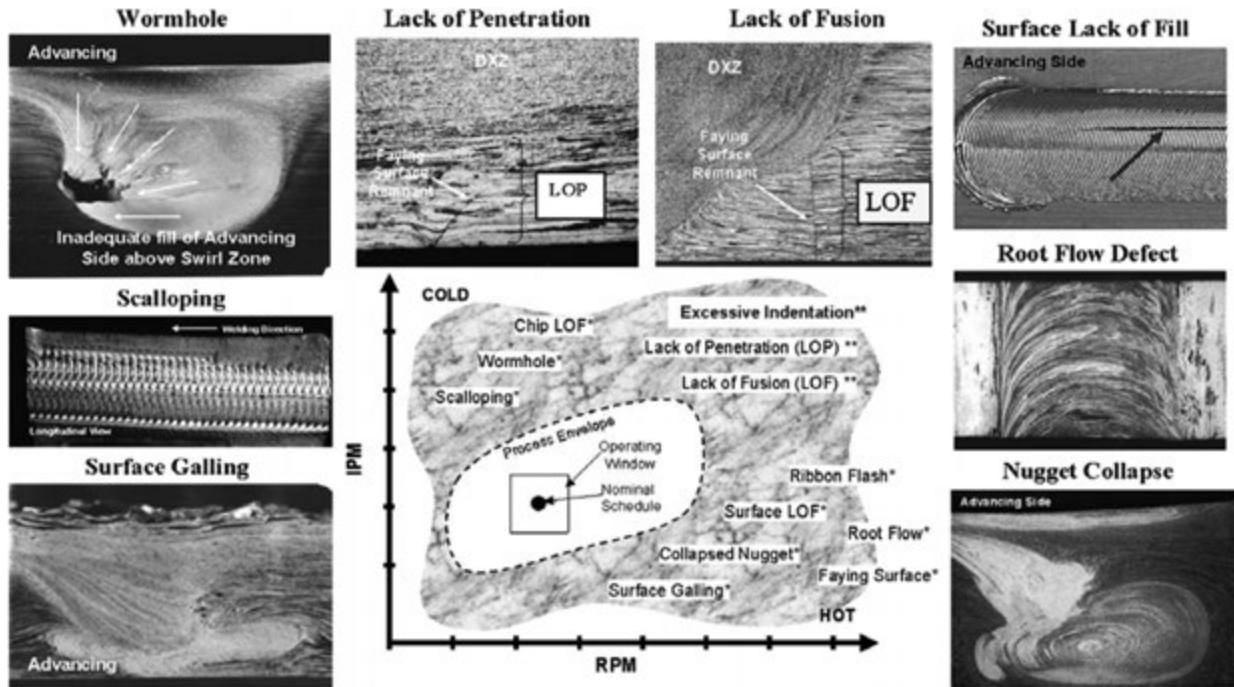


Fig. 6 Different defects appeared in surface composites produced by FSP. Reproduced with permission from Arbegast, W.J., 2003. Hot Deformation of Aluminum Alloys III. Warrendale, PA: TMS, p. 313.

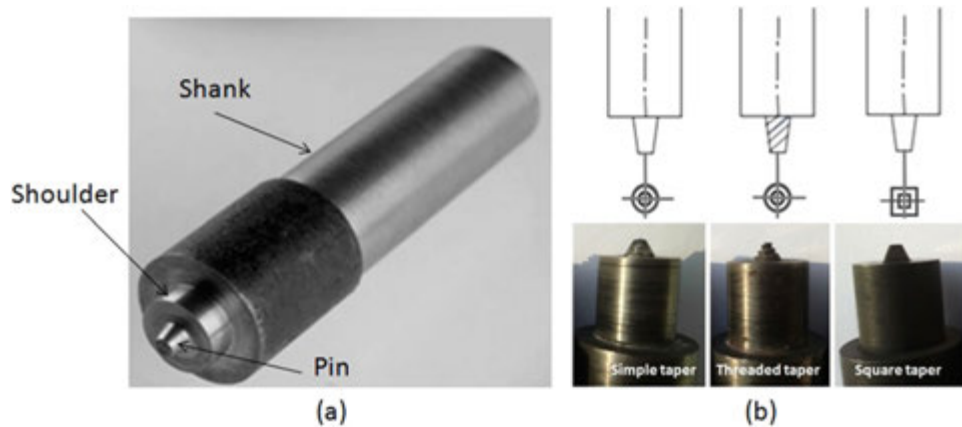


Fig. 7 (a) Typical photograph showing FSP tool, (b) schematic representation and photographs of FSP tool with different pin profiles. Reproduced with permission from Patle, H., Dumpala, R., Ratna Sunil, B., 2018. Machining characteristics and corrosion behavior of grain refined AZ91 Mg alloy produced by friction stir processing: Role of tool pin profile. Transactions of the Indian Institute of Metals 71 (4), 951–959.

The material flow within the stir zone is significantly influenced by the tool pin profile. Several pin designs with different cross sections of square, triangular, cylindrical, and conical with or without threads are used. Some pins also contain special flutes on the surface to increase the rate of the material flow. Simple cylindrical and cone probes with threads and without threads are the most widely used probe designs. By providing more sharp edges for example in the case of probes with square and triangular cross section, the amount of material which is stirred in the nugget zone is increased. By providing threads and flutes, the rate of material flow can be increased as the threads and flutes facilitates more material flow through the channels provided in the form of threads and flutes from the bottom of the workpiece towards the tool shoulder. Therefore, selecting proper tool probe design is crucial in FSP. **Fig. 7** shows photographs of a typical FSP tool used to develop surface composites and different pin profiles with taper and threads provided on the surface. Different types of tool shoulders are used in FSP by considering outer surface, end surface and the end profile as the three important factors. There are three types of shoulder end surfaces which are flat, concave and convex type as shown in **Fig. 8(a–c)**. Flat end shoulder is the simple and most widely used design. However, it is less effective in holding the plasticized material during FSP and results in excess amount of material flash. To address this limitation, concave end shoulder is

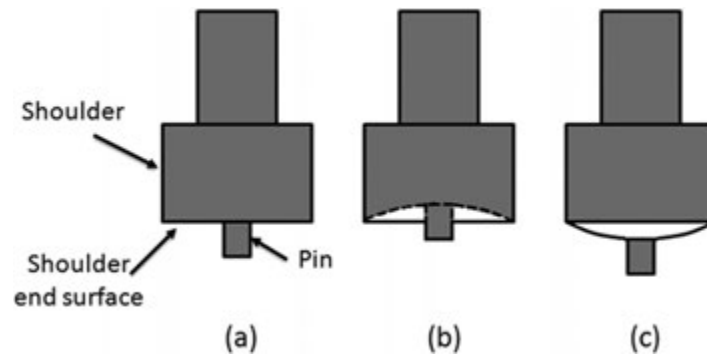


Fig. 8 Schematic representation of tool shoulders: (a) flat end surface, (b) concave end surface, and (c) convex end surface.

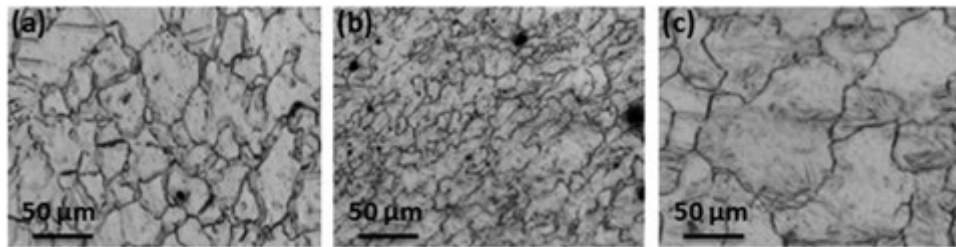


Fig. 9 Microstructural observations of AZ31 Mg alloy: (a) as annealed condition, (b) in the stir zone of FSPed AZ31, and (c) at the bottom of the stir zone in the FSPed AZ31.

suggested. The concave end provides a reservoir of cavity for the flowing material due to the stirring action of the pin beneath the shoulder and avoids the escape of the plasticized material in the form of flash. Convex type shoulder end is another design demonstrated by The Welding Institute (TWI) during the early years of the evolution of friction stir welding. The results were not as expected and the design was less seen in the literature in connection with FSP. The main limitation is the excess amount of material flash. However, a few studies demonstrated the use of convex type end surface particularly in friction stir welding.

Operational Parameters

Other processing parameters which can be seen as operational parameters such as tool rotational speed, travel speed, tool penetration depth, and tilt angle influence the heat generation, heat dissipation, and cooling rate during FSP. Tool rotational speed influences the heat generation to a great extent. Higher tool rotational speeds generate more heat due to higher amount of friction and vice versa. The generated heat plays a crucial role on material flow mechanism and also further influences the level of grain refinement. Recrystallization during plastic deformation known dynamic-recrystallization is the prime reason behind the grain refinement after FSP (Mishra and Ma, 2014). On the other hand, the generated heat is insufficient to plastically deform the material at the lower tool rotational speeds. This in fact leads to formation of tunneling defect. In order to eliminate the tunneling defect, tool rotational speeds can be increased but other adverse effects may result such as (1) grain growth, (2) narrowed nugget zone width, and (3) coating of workpiece material to the tool shoulder. In our earlier work (as shown in Fig. 9), different grain sizes at the bottom of the nugget zone due to the difference on the heat generation and heat dissipation while processing AZ31 Mg alloy by FSP was observed (Saikrishna *et al.*, 2016). It is noted that obtaining optimum tool rotation speed is crucial to achieve grain refinement in FSP. The second undesired result is the affected stir zone width. The width of the stir zone is decreased with increased tool speeds due to the limited amount of material stirring around the tool pin.

Coating of the base material to the tool shoulder is third abnormal affect resulted due to higher tool rotational speeds. Due to higher generated heat, the material in the stir zone reaches soft state and can be easily transferred to the surface of the tool shoulder. Fig. 10 shows the photographs of AZ31 Mg alloy during FSP and after FSP. The plasticized material from the stir zone (Fig. 10(b)) was coated on the surface of the shoulder of the FSP tool. Then, the accumulation of the coated material was unable to bond for longer time and deposited back to the workpiece as observed after FSP (Fig. 10(c)). This deposition led to develop defective stir zone at the end of the process.

Tool travel speed is another important operational parameter that influences the successful formation of a surface composite during FSP. Once the rotating FSP tool is plunged into the workpiece and for some time to stabilize the heat generation, then the rotating tool is given a traverse motion with a suitable speed. The amount of rate of heat generation depends on the tool rotational speed and the amount of heat concentration and dissipation depend on tool travel speed. Lower tool travel speeds facilitates to

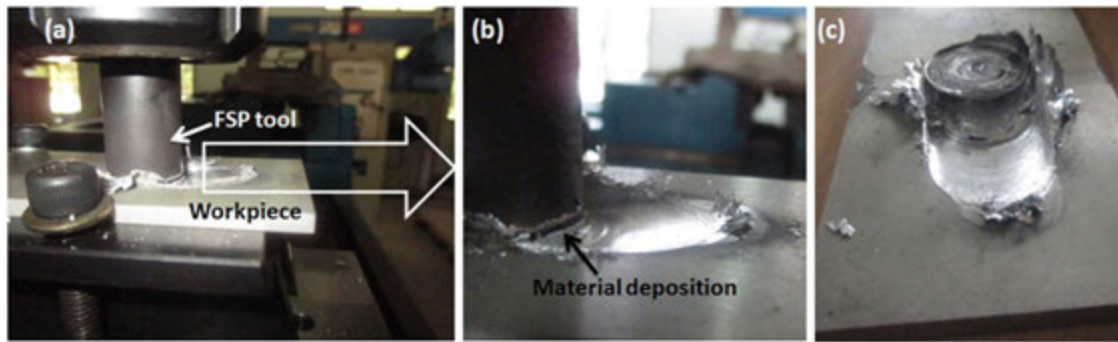


Fig. 10 Photographs showing FSP of AZ31: (a) processing, (b) material deposition, and (c) resulted stir zone. Reproduced with permission from Kondaiah, V.V., Pavanteja, P., Afzal Khan, P., *et al.*, 2017. Microstructure, microhardness and wear behavior of AZ31 Mg alloy – fly ash composites produced by friction stir processing. *Materials Today: Proceedings* 4, 6671–6677.

concentrated more amount of heat in the stir zone and higher tool travel speeds causes more heat dissipation. Obviously, fine grains are resulted with higher tool travel speeds due to lower heat concentration but the occurrence of defects is higher due to poor material flow. Therefore, an optimum combination of tool rotational speed and travel speed is in a great need to eliminate defects and to achieve grain refinement.

Initially during FSP, the rotating FSP tool is appropriately penetrated into the surface of the workpiece and allowed to stir up to certain dwell time before the tool is plunged along the traverse direction. In order to generate sufficient amount of heat, establishing appropriate contact between the tool shoulder and the workpiece surface is crucial. Otherwise, the rotating pin simply produces a groove instead of stirring the workpiece material around it. Therefore, providing appropriate penetration depth of the FSP tool is crucial to produce surface composites without defects. Excess tool penetration gives more flash which is not desired. Along with optimizing the tool rotational and traverse speeds, adopting sufficient tool penetration is important. Tool tilt angle is the angle measured between the axis of the FSP tool and the axis perpendicular to the surface of the workpiece. Tool tilt is crucial particularly, when the shoulder is concave type in achieving appropriate material flow beneath the shoulder. Tool tilt facilitates the stirring material to be confined under the shoulder as the tool travels during FSP. However, by using other kinds of shoulder designs, without tool tilt FSP can be successfully carried out. Usually, the tool tilt angle is maintained from 0° to 3° . Preheating the workpiece materials reduce the required load to initiate the plastic deformation during FSP. Particularly, while processing materials of high melting temperature such as steels and titanium alloys, preheating the workpiece offers several advantages. Furthermore, materials of higher heat conductivity such as copper based materials also give better processing results by preheating. Heating decreases the yield strength of a material and therefore at lower loads material can be easily deformed to modify the microstructure. In addition, the preheating of work piece increases the tool travel speed and decreases the tool wear. By providing preheating to the workpiece, tool wear in the initial stage of process can be reduced. Understanding the role of each process parameter is important before designing FSP experiments for a given material system.

Advantages and Limitations

Surface composites have been produced by FSP by using several pure metals and alloys as matrix materials. Majority of work has been done to develop aluminum alloys, magnesium alloys, titanium, and steels based surface MMCs by incorporating wide range of dispersing phases such as SiC, TiC, Al_2O_3 , TiO_2 , SiO_2 , B_4C , CNT, Graphene, Hydroxyapatite, etc. Furthermore, due to the generated heat during FSP, in-situ surface composites were also developed by accelerating the chemical reaction in the matrix material. Additionally by incorporating two or more phases, hybrid composites were also developed by FSP. Being a solid state processing technique, FSP offers many advantages in producing surface composites compared with other processing routes as given below:

- (1) Compared with melting and solidification routes, phase stability of composite material is higher during FSP.
- (2) FSP doesn't results workpiece melting. Therefore, the oxidation problem and formation coarse grains during the solidification of the liquid metal can be eliminated.
- (3) Developing surface composites by FSP can be achieved by using simple equipment such as automated vertical milling machines which are readily available in the industries with a few modifications.
- (4) Heat generated during FSP can be easily dissipated through the workpiece. The base material area is relatively larger compared with the area of the processed zone and therefore, acts as sink. Thermal stresses which arise during FSP are minimum compared with other conventional methods.
- (5) At controlled parameters, fine grains can be produced in FSPed along with fabricating the composite or developing alloy phases at the surface. The combined advantage of grain refinement and particle dispersion can be achieved by FSP.

- (6) The surface composite produced by FSP exhibits better mechanical properties due to grain boundary strengthening and particle dispersion strengthening.
- (7) FSP can be automated by using robotics and control systems which improves the efficiency of the process.

Although it has been well established the viability of FSP to develop surface composites within the solid state, still the technique suffers from a few limitations and challenges as given below:

- (1) Optimizing the process parameters is required for every material system.
- (2) The surface that is processed by FSP is smaller in area compared with other routes. Multiple adjacent FSP passes may be required to increase the processed area.
- (3) Poor control over the quantity of the dispersing phase. Developing composites of specific composition is difficult as the distribution of reinforcement is non uniform with single pass and multi pass FSP is needed to improve the uniformity in the particle dispersion.
- (4) Different zones are resulted in FSPed zone with different level of grain refinement.
- (5) Flat surfaces are best suitable to produce surface composites by FSP compared with concave or convex surfaces.
- (6) The thickness of surface composite layer that is produced in FSP is limited to few millimeters and depends on the FSP tool pin profile.
- (7) Most of the dispersing phases are hard and brittle, FSP tool wear is usually observed after the process which influences the success of the composite formation.

Conclusions

Developing surface composites within the solid state by FSP has been proven as a promising strategy in the surface engineering. The fundamental mechanisms involve localized heating, extrusion, forging followed by cooling during the material flow while incorporating reinforcements in FSP. Several strategies have been demonstrated to introduce secondary phase particles into the surface which include groove filling, holes filling, sandwich method, surface coating, and direct FSP tool route. Among all of the routes, groove filling has been shown to produce surface composites with higher thickness. The advantage of grain refinement and presence of secondary phase in the surface composites produced by FSP enhance mechanical and wear properties. However, corrosion properties of these composites are material dependent and hence, care must be exercised in selecting the secondary phase. Furthermore, a few special properties such as surface wettability and bioactivity also can be improved by incorporating suitable reinforcements at the surface by FSP. Among all the tool design parameters and process parameters, tool shoulder and pin dimensions, rotational and travel speeds play crucial role. Adopting FSP to develop surface composites with a set of optimized tool design and process parameters certainly help to develop surface composites with hybrid properties. Even though, multiple number of FSP passes increases the level of secondary phase distribution in the composite, increased number of FSP passes increases the processing time and cost. Hence, detailed research is still in need, to address the existing challenges to achieve higher level of homogeneity in the particle distribution throughout the stir zone. Furthermore, development of new tool designs to process non-flat surfaces with concave or convex geometries is also in a great need. After all, the friction based processes including FSP are at their infant stage compared with the conventional composite fabrication processes. The advent of automation and robotics in the manufacturing sector helps adopting FSP to develop surface composite layers with precise control and dimensions. From the overall observations, it can be learnt that FSP can be a promising solid state route to develop surface composites with improved properties. Furthermore, with lower level of modifications to the existing equipment, FSP can be readily adopted by the manufacturing industry particularly in the fields of surface engineering.

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Further Reading

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Magnesium-Based Composites for Degradable Implant Applications

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Abbreviations

EDS energy dispersive X-ray spectroscopy
FSP friction stir processing
HA hydroxyapatite
Mg magnesium

SAED selective area electron diffraction
SEM scanning electron microscope
TCP tricalcium phosphate
TEM transmission electron microscope

Glossary

Bioactivity Ability of the material to bond with the host tissue.

Biocompatibility Ability of the biomaterial to be accepted and tolerated by the human body.

Biodegradability Ability of the material to be degraded safely without leaving any harmful residues.

Cytotoxicity Localized toxic effect of the implant material on the host tissue.

Osseointegration Developing structural and functional bonding between the tissue and the surface of the implant.

Stress shielding A phenomenon by which fractured bone experiences lower stresses when supported with an implant material of higher young's modulus.

Introduction

Biomedical engineering has witnessed several radical changes in the past five decades in understanding and developing new age biomaterials intended to be used as implants to support, replace, or enhance the function of an existing human organ. Development of bioactive and biodegradable materials to replace early generation bioinert materials is one of such best examples which revolutionized the applications of metals, ceramics, polymers, and composite materials in the medical industry (Park and Lakes, 2007). Among these notable advances, research on developing degradable metals including iron (Fe)-based and magnesium (Mg)-based alloys for cardiovascular and orthopedic applications has become one of the potential and attractive research areas for the past two decades (Kirkland and Birbilis, 2014). Iron-based alloys have been widely investigated for degradable stent applications and Mg-based alloys were investigated for both the stents as well as for load bearing orthopedic implant applications (Hermawan *et al.*, 2010). It is important to note that the available medical grade steels, titanium and its alloys, and Co–Cr alloys have been approved and well established as candidates to manufacture various implants (Park and Lakes, 2007). For permanent implants, where the support of the biomaterial is necessarily required for a patient for the entire life span, biodegradable materials are not a replacement or an alternate solution. Biodegradable implants are targeted for temporary applications where the support of the implant is required for certain duration until the deceased or fractured tissue/organ is sufficiently healed. Then the implant is slowly degraded in the physiological environment and disappeared without causing any health abnormalities during the degradation process. Mostly, the degradation is a result of chemical breakdown of the material in the aggressive physiological environment (Kirkland and Birbilis, 2014; Hermawan *et al.*, 2010). It is a prerequisite for any material to be used as biodegradable material for medical applications that the corrosion by-products must not cause toxicity or any other health issues.

Magnesium as a Biomaterial

In recent years, magnesium has become the promising choice of material system to develop degradable load-bearing orthopedic implants due to excellent biocompatibility and non-toxicity (Witte *et al.*, 2008). Being a light metal, Mg has mechanical properties close to that of natural human bone, which also offer additional advantage to address the stress shielding effect; a common phenomenon arises due to mismatch between the Young's modulus of the bone and the implant material. However, besides all these advantages, rapid degradation of Mg in the biological environment is the important limitation that must be addressed to develop Mg-based degradable implants (Witte *et al.*, 2008; Zeng and Dietzel, 2008). Mg degrades rapidly due to biocorrosion in the physiological environment (Wang *et al.*, 2008). The rate of new bone formation is inferior compared with the rate of mass loss of the Mg implant due to biocorrosion. Therefore, a clear gap is developed between the corroding Mg implant and the surface of the new bone tissue as schematically shown in Fig. 1(a), which adversely affects the mechanical integrity of the implant with the tissue.

During the initial days of healing process, the bone remodeling rate to form new tissue is lower. After a few weeks, the rate of new bone formation is significantly increases and further again decreases at the end of the healing process as schematically

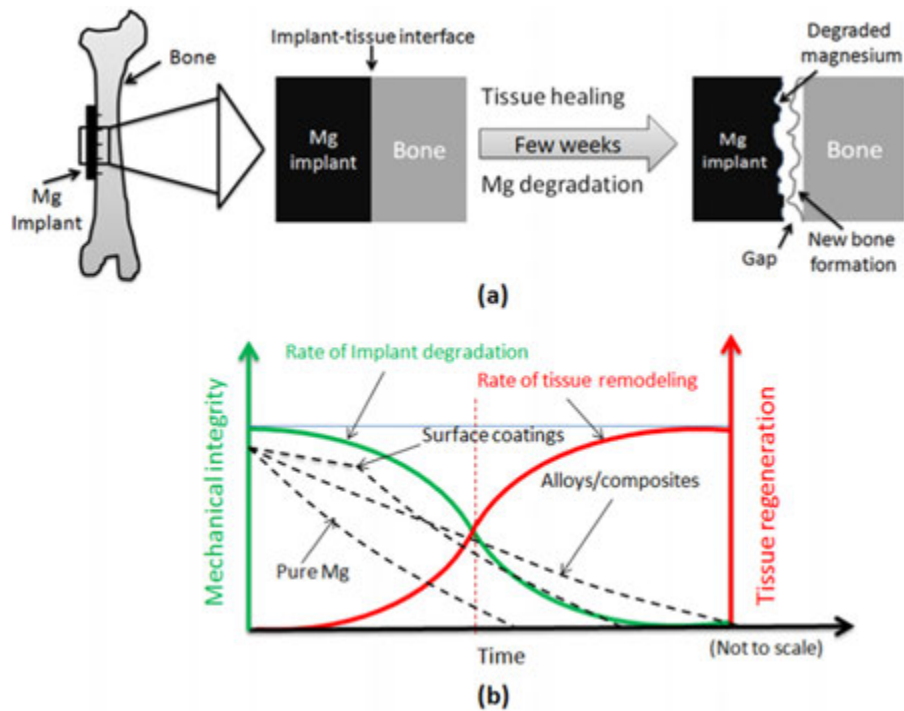


Fig. 1 Schematic representation of degradation of Mg-based implants: (a) Implant-tissue interface and (b) comparing the healing rate of fractured bone tissue and the desired rate of degradation of the ideal implant.

illustrated in [Fig. 1\(b\)](#). Ideally, Mg implant should provide support without losing its mechanical integrity with the tissue. Pure Mg rapidly undergoes degradation before the deceased or fractured bone gets sufficiently healed. Several strategies such as adding different alloying elements to Mg, producing Mg-based composites, providing surface coatings, and microstructural modifications ([Kirkland and Birbilis, 2014](#); [Hermawan et al., 2010](#); [Shaylin and George, 2012](#); [Sigrid et al., 2011](#); [Hornberger et al., 2012](#); [Ratna Sunil et al., 2014b](#)); have been adopted and extensively studied, understood, and demonstrated the efficacy of these routes to tailor Mg and its alloys for medical applications. Different Mg-based composites were developed through several liquid state and solid state processing routes and the properties and suitability of these composites as degradable biomaterials have been investigated. Decreasing the degradation rate by providing surface coatings on Mg alloy offers excellent corrosion resistance and improved surface functionalization to tailor the implant with higher bioactivity. However, the performance of the surface coating is limited to shorter duration. If the substrate is exposed to the corroding physiological environment, degradation accelerates and the bonding strength between the coating and the Mg implant decreases. Then, the degradation rate gradually increases and the surface coating becomes ineffective. Instead of providing a bio-functionalized coating on the surface, if the substrate is modified in terms of physical and chemical response to the physiological environment, better degradation control can be achieved as long as the material is remained till the degradation process is slowly completed. Here comes, the necessity of adding secondary phases which are biocompatible and can promote special properties to the matrix. Furthermore, the selection of Mg alloy as matrix material is also crucial as the alloy must be non-toxic and well tolerated by the human body.

Magnesium-Based Composites for Implant Applications

Composite materials contain multi-phases which are physically and chemically distinct and offer hybrid properties resulted from their constituting phase properties. Human bone itself is a composite material mainly composed of hydroxyapatite ceramic crystals at nano-scale, collagen, proteins, and other growth factors along with living tissue. Different properties can be couples by producing composites. The behavior of the composite depends on the properties of its basic constituting elements. Adding bioactive ceramic phases to Mg to enhance bioactivity, corrosion resistance, and promote better tissue interactions is a very good example to understand the potential of composite materials to deliver hybrid properties for medical applications.

Matrix and Reinforcements

Developing Mg alloys for medical applications is complex as the properties of alloys are governed by the alloying elements. In this context, the selection of an Mg alloy as matrix material is vital to successfully produce a composite for medical applications. Alloying elements directly influence mechanical, corrosion, and toxic properties of the material. If the level of addition of alloying element is

Table 1 Toxicity effects of important alloying elements in Mg based alloys

Element	Daily allowable dosage (mg)	Natural presence of an element in the human body (g)	Toxicology	References
Mg	400	25	Turmoil in Mg homeostasis causes nausea, kidney failure, and ineffective breathing	Agarwal <i>et al.</i> (2016), Chen <i>et al.</i> (2016b)
Ca	1400	1100	Kidney stones, Hypoparathyroidism, and heart problems	Agarwal <i>et al.</i> (2016), Chen <i>et al.</i> (2016b)
Al	14	< 0.3	Toxicity to neurons, Alzheimer disease, excess in bone results lower osteoclast viability	Agarwal <i>et al.</i> (2016), Chen <i>et al.</i> (2016b)
Zn	15	2	High contents lead to neurotoxicity, muscle cramp, and diarrhea	Agarwal <i>et al.</i> (2016), Chen <i>et al.</i> (2016b)
Mn	3.5	0.012	High contents result in psychiatric issues and motor disturbances	Agarwal <i>et al.</i> (2016), Chen <i>et al.</i> (2016b)
Cu	6	–	Excess amount causes kidney impairment and ineffective breathing	Schroeder <i>et al.</i> (1966)
Zr	3.5	< 0.250	Cationic form leads to accumulation on bones	Agarwal <i>et al.</i> (2016), Chen <i>et al.</i> (2016b)
Li	0.2–0.6	–	Result in higher alkalization of the body fluid	Agarwal <i>et al.</i> (2016), Chen <i>et al.</i> (2016b), Gu and Zheng (2010), Song and Song (2007)
Be	0.01	–	May cause lung cancer	Agarwal <i>et al.</i> (2016), Chen <i>et al.</i> (2016b)
Fe	10–18	–	Diseases related to human age due to reactive O ₂ species	Gu and Zheng (2010)
Si	24–33	–	High contents of SiO ₂ causes lung diseases	Fishbein (1984)
Ni	0.6	–	Causes skin allergies, lung fibrosis, kidney and heart problems	Denkhaus and Salnikow (2002)
Sn	3.5	–	Skin and eye irritation	Winship (1988)
Sr	5	–	Leads to hypocalcemia because of increased Ca kidney excretion	Morohashi <i>et al.</i> (1994), Posner (1982)
RE (Ce, La, Nd, Pr, Y)	4.2 (combined)	–	Sc (non-toxic), Y (mildly toxic), La (low blood pressure etc.), Ce (Cardiovascular disease, etc.), Pr, Tb, Er, Ho, Tm, Lu and Nd (moderate toxic), Pm (non-toxic), Sm (non-toxic insoluble salts but slight toxic soluble salts), Eu (no clear toxic indication), Gd, Yb (highly toxic)	Chen <i>et al.</i> (2016b), Rim <i>et al.</i> (2013)

Note: Ali, M., Hussein, M.A., Al-Aqeeli, N., 2019. Magnesium-based composites and alloys for medical applications: A review of mechanical and corrosion properties. *Journal of Alloys and Compounds* 792, 1162–1190.

within the solubility limit, solid solution grains may be resulted. With the higher amounts of alloying elements, intermetallics are likely to form which are hard, brittle, and difficult to separate from the matrix. These intermetallics exhibit different electro-chemical events compared with the other regions of the alloy. Therefore, selection of Mg alloy matrix is crucial to develop Mg-based composites for medical applications. Usually, elements such as Al, Zn, Zr, Y, Cu, Cd, RE, Li, Mn, Pb, Ag, Cr, Si, Sb, Ba, Th, V, Ce, La, Co, Sn, etc., are used as alloying elements to develop Mg-based alloys (Ali *et al.*, 2019). However, every alloy cannot be suitable as matrix material due to biocompatibility issues. A few elements may be tolerated up to a minor level and become toxic beyond the limits. Table 1 lists most important alloying elements usually used in Mg alloys and their toxic effects on healthy tissue.

Several reinforcing materials have been used to produce Mg composites for biomedical applications. Ceramic materials and metallic powders including ZrO₂, Al₂O₃, TiO₂, ZnO, MgO, TiB₂, SiO₂, TiC, TiN, Si₃N₄, CNTs, Zn, Sr, Zr, Sr, Ti, hydroxyapatite, tricalcium phosphate, etc., can be used as reinforcements to develop Mg-based composites (Ali *et al.*, 2019). Table 2 lists different ceramic materials used for biomedical applications.

Hydroxyapatite (HA) with chemical formula Ca₁₀(PO₄)₆(OH)₂ has close chemical composition of calcium phosphate mineral phase of natural bone that can be a potential reinforcement to develop biodegradable Mg-based composites. HA exhibits excellent biocompatibility, bioactivity, and osseointegration. By adding HA to Mg, increased biomineralization can also be achieved which further protects the Mg substrate from aggressive corrosion in the physiological environment. It has been well demonstrated that the addition of HA enhances mechanical, corrosion and bio-properties of Mg-based composites (Gu *et al.*, 2010; Khalil and Almajid, 2012; Khanra *et al.*, 2010; Sun *et al.*, 2014; Viswanathan *et al.*, 2013; Witte *et al.*, 2007; Ye *et al.*, 2010; Zhao *et al.*, 2011). Adding more HA also enhances the tissue interactions at the surface of the implant and improves the healing rate. In the context of bio-properties, more amounts of HA may provide favorable conditions. However, on the other hand, mechanical and corrosion properties are deteriorated with increased HA content. The presence of any secondary phase beyond certain levels in Mg introduces higher galvanic corrosion as the reinforcement is treated as an impurity (Song and Atkins, 1999). Therefore, a limitation to the

Table 2 List of ceramic materials and their properties used for biomedical applications

Materials	Types and characteristics	Properties	Medical applications
Alumina (Al_2O_3)	Bioinert and biocompatible	Extremely hard, high wear resistance, high strength and stiffness (Parikh, 1995; Roy <i>et al.</i> , 2005)	Bone replacement, hip prostheses, maxillofacial prostheses, ossicular chain fixation, keratoprosthesis and dental implants (Mohanty, 1995)
Zirconia (ZrO_2)	Bioinert and biocompatible and non-toxic	High elastic modulus, high fracture toughness, high wear resistance, high flexural strength (Ravi Kumar <i>et al.</i> , 2018; Radha and Sreekanth, 2017)	Hip replacement, ceramic crowns, endosseous implants and implant abutments (Chen <i>et al.</i> , 2016a)
Titania (TiO_2)	Bioinert, biocompatible, low toxicity (Meenashisundaram <i>et al.</i> , 2015)	Excellent mechanical durability, high transparency in visible regions (Chuang <i>et al.</i> , 2011)	Photodynamic therapy treatment, drug delivery systems, cell imaging and biosensors (Fei Yin <i>et al.</i> , 2013)
Zinc oxide (ZnO)	Biodegradable, biocompatible, low toxicity (Zhang <i>et al.</i> , 2013)		Anticancer, antibacterial fields, antidiabetic treatment, biomedical imaging, wound healing and anti-inflammation (Jiang <i>et al.</i> , 2018)
Magnesium oxide (MgO)	Bioglass, biocompatible	Improves mechanical properties and corrosion resistance of Mg	Antibacterial function (Lei <i>et al.</i> , 2012)
Titanium diboride (TiB_2)	Bioinert, biocompatible	High hardness, high elastic modulus, high wear resistance, high corrosion resistance (Meenashisundaram <i>et al.</i> , 2014)	Dental implants, fibroblast attachment (Makau <i>et al.</i> , 2013)
Silicon dioxide or silica (SiO_2)	Bioglass, Bioactive, biocompatible, non-toxic (Haghshenas, 2017)	Improves hemocompatibility (Walke <i>et al.</i> , 2016), improves corrosion resistance, brittle, not suitable for load bearing applications (Bommala <i>et al.</i> , 2019)	Dental implants, drug delivery, bone tissue regeneration (Haghshenas, 2017), biomedicine (Vallet-Regí and Balas, 2008)
Hydroxyapatite (HA) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	Bioactive, excellent biocompatibility, biodegradable	Stable in the physiological environment	Orthopedic implants, dental implants, metallic implant coatings, drug and gene delivery, and tissue engineering scaffolds (Mucalo, 2015)
Tricalcium phosphate	Biodegradable		Bone tissue regeneration (Canillas <i>et al.</i> , 2017)

Note: Ali, M., Hussein, M.A., Al-Aqeeli, N., 2019. Magnesium-based composites and alloys for medical applications: A review of mechanical and corrosion properties. *Journal of Alloys and Compounds* 792, 1162–1190.

quantity of HA is necessarily drawn in developing Mg-based composites to reduce the galvanic affect. Adding more amount of ceramic phase in metallic system leads to increase brittleness and deteriorate mechanical performance. Therefore, choosing an optimum amount of HA as dispersing medium is crucial. A brief summary of work done in developing Mg-based composites by incorporating calcium phosphate mineral phases for biomedical applications is given in Table 3 (Vandana *et al.*, 2019). Another interesting development is using naturally derived nano-HA to develop Mg composites. Fish bone derived HA has been used in couple of studies (Vandana *et al.*, 2019; Praveen Kumar *et al.*, 2019) and improved bioactivity and corrosion resistance was observed. Fig. 2 shows photograph of the fish bones and electron microscope image of nano-HA derived from these fish bones and the cross-section of the produced composite by using ZE41 Mg alloy as the matrix through friction stir processing route (Ratna Sunil and Jagannatham, 2016). However, the addition of HA decreases the mechanical properties in Mg–HA composites which must be carefully noted (Gu *et al.*, 2010; Khanra *et al.*, 2010). Hence, care must be exercised to select the amount of HA reinforcement to not to deteriorate mechanical behavior at the cost of improving the bioactivity and corrosion resistance.

Processing Routes to Develop Mg Composites

There are a few well-known processing routes adopted to develop Mg-based composites. Among them, powder metallurgy, casting, and friction stir processing are most widely used methods as discussed here. Powder metallurgy is one of the widely used processing routes to develop composites. In powder metallurgy, matrix material and the dispersing reinforcements are blended in appropriate ratios and then compacted to consolidate the powder mixture by applying a suitable load. The component that is produced after compaction is called as green compact. Then sintering is carried out at appropriate temperature to complete the process. Usually, sintering temperatures are more than 0.5 times of base material melting point. In powder metallurgy, blending is crucial to uniformly disperse the reinforcement throughout the composite. Adopting advanced powder processing routes such as ball milling helps to blend the composite powders properly. Additionally, particle size and morphology can also be completely altered with high energy ball milling. Fig. 3 shows TEM image of Mg particle coated with nano-HA crystals after high energy ball milling and sintered compacts (Ratna Sunil *et al.*, 2014a). Achieving such a uniform distribution at the level of each Mg particle helps to develop Mg-based composites with uniform distribution of the reinforcement.

Table 3 A brief summary of work done to develop Mg-based composites by dispersing HA for biomedical applications

Composite	Processing route	Significant findings	Authors
AZ91D Mg alloy–20% HA	Powder metallurgy	● Enhanced corrosion resistance in artificial sea water and cell solutions	Witte <i>et al.</i> (2007)
AZ91 Mg alloy–20% fluorapatite	Powder metallurgy	● Better mechanical behavior, decreased corrosion rate and improved rate of apatite formation in simulate body fluids	Razavi <i>et al.</i> (2010)
Pure Mg–HA (5, 10% and 15%)	Melting and extrusion	● Reduced tensile strength and compressive strength with the addition of HA	Khanra <i>et al.</i> (2010)
Pure Mg–HA (10, 20% and 30%)	Powder metallurgy	● Decreased strength, ductility, corrosion resistance with the increase of HA content	Gu <i>et al.</i> (2010)
Mg–Zn–Zr alloy–nano-HA	Melting and extrusion	● The cytotoxicity evaluation showed non-toxicity to L-929 cells	Ye <i>et al.</i> (2010)
Mg–6% Zn alloy–5% HA	Powder metallurgy	● Improved corrosion resistance and in vitro cytocompatibility	Zhao <i>et al.</i> (2011)
Pure Mg–1% HA	Powder metallurgy	● Improved mechanical and corrosion properties	Khalil and Almajid (2012)
		● The relative density, microhardness, compressive strength and crystal size increased with increasing sintering time temperature and then decreased with increasing sintering time	
Pure Mg–HA (10% and 20%)	Plasma electrolytic oxidation (PEO)	● Decreased corrosion resistance with increase in HA content after spark plasma sintering	Viswanathan <i>et al.</i> (2013)
		● Corrosion resistance was improved after PEO and composite with 10% HA shows better performance compared with 20% HA	
Mg–3Zn–0.5Zr alloy–HA (0, 0.5, 1% and 1.5%)	Melting	● Improved mechanical properties for Mg–3Zn–0.5Zr/1.5HA composite	Sun <i>et al.</i> (2014)
Pure Mg–nano-HA	Friction stir processing	● Mg–3Zn–0.5Zr/1HA composite exhibited lower corrosion rate	
AZ31 Mg alloy–nano-HA	Friction stir processing	● Increased wettability, bioactivity, biomineralization and cell adhesion due to HA	Ratna Sunil <i>et al.</i> (2014c)
		● Refine microstructure due to presence of nanoHA	Ratna Sunil <i>et al.</i> (2014b)
		● Lower degradation in simulated body fluids	
Mg–HA (8, 10% and 15%)	Ball milling and spark plasma sintering	● Enhanced biomineralization and cell adhesion on the composite	
		● Optimum composition was measured as Mg – 10% HA with better hardness, fracture toughness and corrosion properties	Ratna Sunil <i>et al.</i> (2014a)
Pure Mg–HA (0, 2, 5, 10%)	Extrusion and spark plasma sintering	● 5wt% HA was found to be optimum composition for better mechanical properties	Kubásek <i>et al.</i> (2015)
AZ91 Mg alloy–porous HA	Squeeze casting	● The composite exhibited higher compressive strength and experienced brittle fracture	Chen <i>et al.</i> (2016c)
Pure Mg– nano/micro HA	blending–cold pressing–hot pressing	● Addition of 3% nano-HA has shown superior mechanical properties compared with micro-HA	Saremi and Kavosi (2017)
Pure Mg–fish bone derived HA	Friction stir processing	● Tensile properties were decreased but corrosion performance was observed as relatively better for the composite	Vandana <i>et al.</i> (2019)
ZE41 Mg alloy – fish bone derived HA	Friction stir processing	● Better corrosion performance for the composite observed in electrochemical tests and immersion tests carried out in simulated body fluids	Praveen Kumar <i>et al.</i> (2019)

Note: Vandana, B., Syamala, P., Sri Venugopal, D., *et al.*, 2019. Bulletin of Materials Science 42, 122.

Casting is the oldest technique used to develop composite materials. In casting route, matrix material is melted and reinforcements are dispersed in the molted condition of the matrix material. In order to uniformly distribute the reinforcement, stirring of the molten metal is essential. Melting Mg is complex due to its highly reactive and inflammable nature. Therefore, under protective environment conditions, Mg melting need to be done carefully followed by addition of the reinforcement. Developing Mg-based composites by casting route is simple and widely known in the manufacturing industry. However, due to the special metallurgical, physical, and chemical properties of Mg and its alloys, developing Mg-based composites through liquid state methods involve the following complexities which must be considered:

- (1) Highly reactive nature of Mg liquid at higher temperature.
- (2) Highly inflammable nature of Mg.
- (3) Issues concerning the stability of the reinforcing material at high temperatures.
- (4) Tendency of the reinforcement to form intermetallic compounds with Mg.
- (5) Agglomeration of the reinforcements. This issue is more common if the reinforcing powder is in the nano-scale level.

Fig. 4 shows the microstructure of HA-reinforced pure Mg and ZM61 Mg alloy composites produced by melting followed by the extrusion method. Presence of magnesium oxide (MgO) is noticed in the composites which is due the reaction happened between HA and Mg during melting as demonstrated by Khanra *et al.* (2010). This is a common finding usually observed in developing Mg-based composites. Either formation of MgO or formation of other intermetallics due to the reaction between the Mg and the dispersed secondary phase is usually observed in casting route.

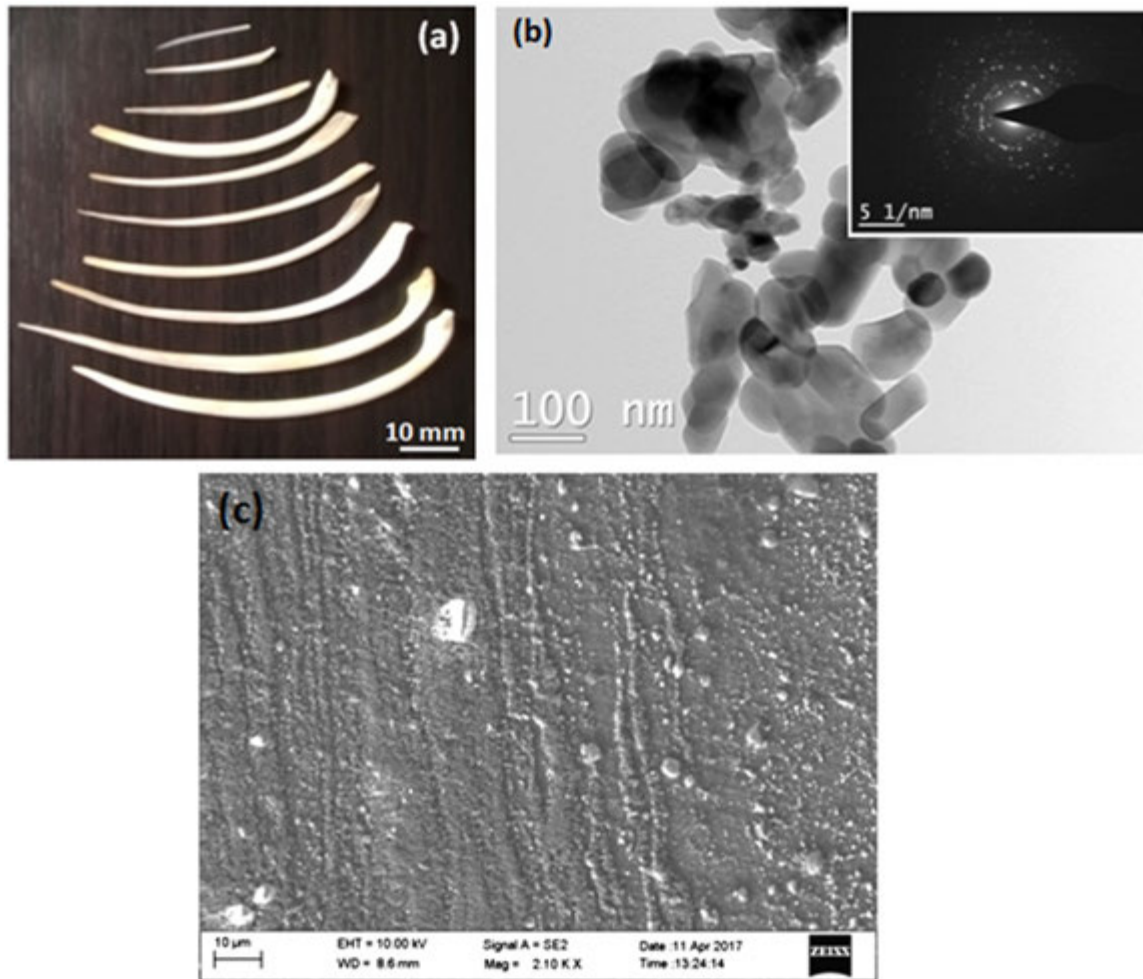


Fig. 2 (a) Photograph of fish bones, (b) transmission electron microscope (TEM) image of produced nano-HA and (c) cross-section of the composite of ZE41 Mg alloy-fish bone derived HA; developed through friction stir processing. *Source:* Ratna Sunil, B., Jagannatham, M., 2016. Producing hydroxyapatite from fish bones by heat treatment. *Materials Letters* 185, 411–414.

Friction stir processing, widely called as “FSP,” is one of the new solid state processing routes by which composite can be produced without melting the base material. In FSP, a rotating non-consumable tool is used to stir the material and caused drastic changes in microstructural features. It was proposed and demonstrated by [Mishra *et al.* \(2003\)](#) that the reinforcement can be introduced into the matrix material during FSP and surface composites can be produced successfully. FSP completely eliminates the issues associated with casting process. Additionally, introduces grain refinement in the composite. Therefore, along with incorporation of the reinforcements, development of fine grains also benefits as the grain size reduction enhances the wettability, a desired property required for biomaterials. [Fig. 5](#) shows typical photographs of the composite and scanning electron microscope observations of AZ31 Mg alloy before and after reinforcing HA by using FSP. [Fig. 5\(b\)](#) confirms the presence of nano-HA (white arrows) from the energy dispersive X-ray spectroscopy (EDS). Grain size reduction, increased surface energy, rapid biomineralization, increased bioactivity, better mechanical properties, and enhanced implant tissue interactions are the advantages with FSP when developing Mg-based composites for biomedical applications ([Ratna Sunil *et al.*, 2012, 2014b,c](#)).

Properties of Mg Composites Influenced by the Reinforcements

When the reinforcement is added to the matrix, its basic chemical composition changes and the properties which are influenced by the physical and chemical characteristics of the constituting phase tend to alter. The addition of reinforcements to Mg and its alloys alter the local distribution of the phases and reflect in terms of bulk behavior of the structure when subjected to mechanical loads, exposed to corroding medium and biological environment.

Controlling the degradation of Mg by decreasing the corrosion rate is prime objective behind developing the Mg-based composites for biomedical applications. Additionally, the embedded particles may enhance other properties such as hydrophilicity, bio-activity,

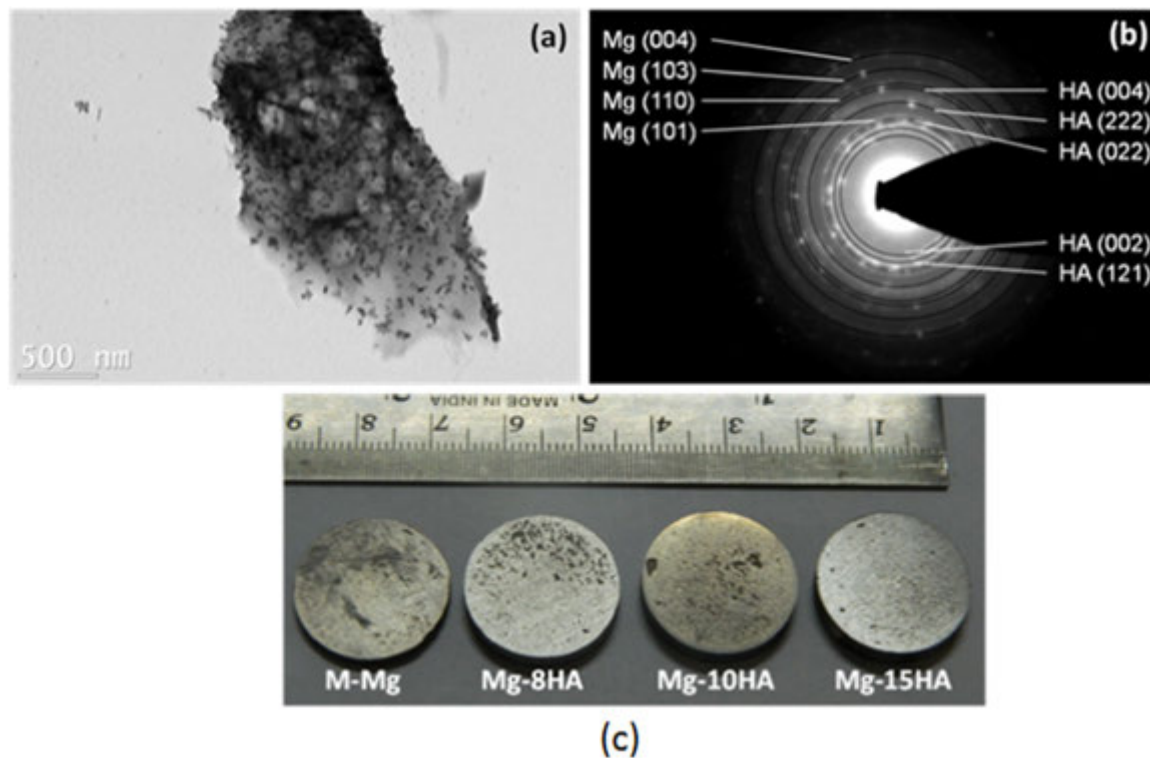


Fig. 3 (a) Transmission electron microscope (TEM) image of Mg particle coated with nano-HA crystals, (b) corresponding selective area electron diffraction (SAED) pattern, and (c) spark plasma sintered compacts of Mg-HA. *Source:* Ratna Sunil, B., Ganapathy, C., Sampath Kumar, T.S., Chakkingal, U., 2014a. *Journal of the Mechanical Behavior of Biomedical Materials* 40, 178–189.

bio-mineralization, etc. All reinforcements which are either ceramics or metallic powders exhibit their own electric potential. Addition of secondary phase particles may locally change the electro-chemical events at the vicinity of the matrix and reinforcement and results in increased or decreased corrosion resistance. If the incorporated reinforcement forms a galvanic cell in the presence of matrix, corrosion rate will be increased. On the other hand, several studies demonstrated improved corrosion resistance by adding reinforcements to Mg. When Mg is exposed to aqueous solution, $\text{Mg}(\text{OH})_2$ forms due to the anodic and cathodic reactions (Song and Atrens, 1999). In the presence of chloride ions, $\text{Mg}(\text{OH})_2$ is unstable and, therefore, MgCl_2 salt tend to form which easily dissolves in the physiological environment. This cycle of degradation by forming $\text{Mg}(\text{OH})_2$ followed by formation of MgCl_2 accelerates the degradation of Mg as schematically explained in Fig. 6(a). Degradation of Mg can be controlled at two stages to increase the Mg implant life span. Initially, by decreasing the formation of $\text{Mg}(\text{OH})_2$ due to corrosion and later, delaying the formation of MgCl_2 crystals, the degradation rate can be reduced and Mg implant life span can be increased. Here comes the advantage of incorporated secondary phase in Mg-based composites. The mechanism behind improved degradation of Mg-based composites incorporated with HA is schematically explained in Fig. 6. When HA (or any other bioactive ceramic powder) is added to pure Mg, rapid biomineralization happens due to the presence of HA crystals in the substrate which act as nucleating sites for mineral depositions. These newly deposited mineral phases along with HA delay the formation of MgAl_2 and helps to decrease the degradation of the composite (Ratna Sunil *et al.*, 2014c).

Mechanical properties will be significantly altered by the size, shape, and quantity of the reinforcements which are added to the matrix. The level of homogeneity in the distribution of reinforcement also influences the bulk properties of the material. Particle dispersion strengthening is the prime mechanism by which the strength of the composite material is increased. However, ductility and toughness of the composite may be decreased due to the addition of the reinforcements. The addition of reinforcements at the nano-scale significantly improves the yield strength and ductility of the composites. Nano-reinforcements such as Al_2O_3 (Pogrebnjak *et al.*, 2006), TiO_2 (Pogrebnjak *et al.*, 2008), Y_2O_3 (Goh *et al.*, 2007), ZrO_2 (Pogrebnjak *et al.*, 2012), ZnO (Meenashisundaram and Gupta, 2015), SiC (Pogrebnjak *et al.*, 2012), TiC (Meenashisundaram and Gupta, 2015), CNT (Goh *et al.*, 2006), hydroxyapatite (Ratna Sunil *et al.*, 2014a) have improved the mechanical behavior of Mg composites. From the aforementioned studies, it can be clearly demonstrated that the size of the reinforcement exhibits significant effect on altering the mechanical properties. Mg composites with nano-reinforcements exhibits relatively better mechanical properties when compared with large particle size reinforcements. As demonstrated by Jaiswal *et al.* (2018), the distribution and the composition play the most important role on controlling the corrosion and achieving the best mechanical behavior of Mg-3Zn-HA composite. Even though, the hardness was measured as higher for 10%HA-reinforced composites, yield strength was observed as better for

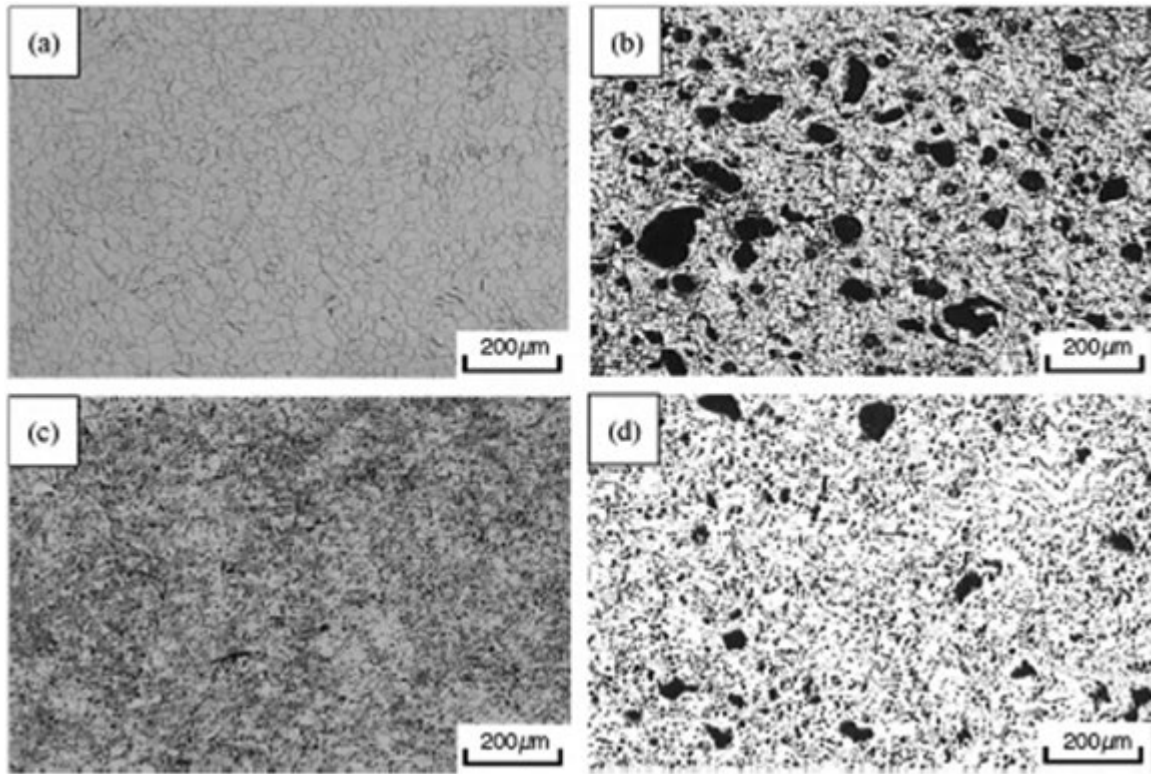


Fig. 4 Microstructure of Mg-based composites: (a) Mg-0%HA, (b) Mg-10%HA, (c) ZM61 Mg alloy-0%HA, and (d) ZM61 Mg alloy-5%HA. Source: Khanra, A.K., Jung, H.C., Yu, S.H., Hong, K.S., Shin, K.S., 2010. Microstructure and mechanical properties of Mg-HAP composites. Bulletin of Materials Science 33 (1), 43–47.

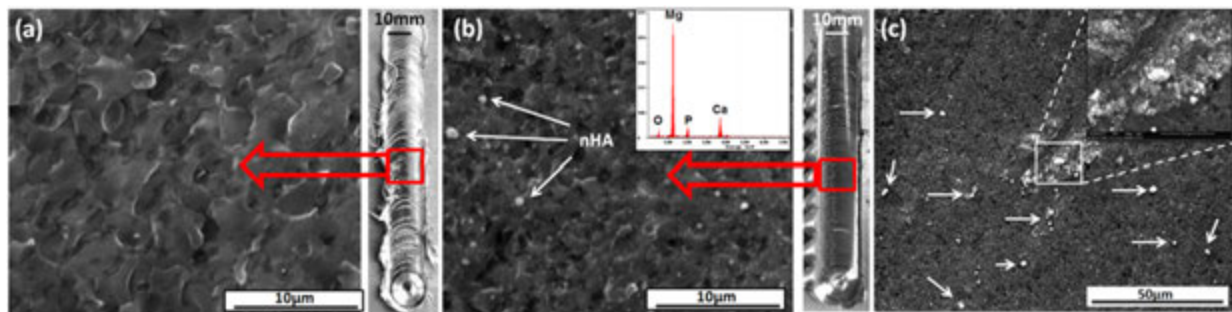


Fig. 5 Scanning electron microscope images of AZ31 Mg alloy before and after incorporating nano-HA through FSP: (a) FSPed AZ31 without nano-HA, (b) AZ31-nanoHA composite at high magnification, and (c) AZ31-nano-HA composite low magnification. Source: Ratna Sunil, B., Sampath Kumar, T.S., Chakkingal, U., Nandakumar, V., Doble, M., 2014. Nano-hydroxyapatite reinforced AZ31 magnesium alloy by friction stir processing: A solid state processing for biodegradable metal matrix composites. Journal of Materials Science: Materials in Medicine 25 (4), 975–988.

5%HA-reinforced composite (as shown in Fig. 7). This is attributed to the poor bonding of 10%HA composite. The bonding strength between the reinforcing particles and the matrix play crucial role on increasing the strength and ductility of the composite.

Increasing the interactions and providing favorable conditions to establish a strong bond between the implant and the local tissue is known as bioactivity. Bioactivity depends on several factors and among them chemical composition and surface energy are the two significant factors directly governs the ability of the implant to form a strong bond with the tissue. Among the available ceramic materials, calcium-phosphate mineral phases such as hydroxyapatite (HA) and tricalcium phosphate (TCP) are good examples which exhibit excellent bioactivity. Adding these calcium-phosphate mineral phases as dispersing particles into Mg matrix alters the surface properties and bioactivity of the composite. It was observed that the addition of nano-HA has profound

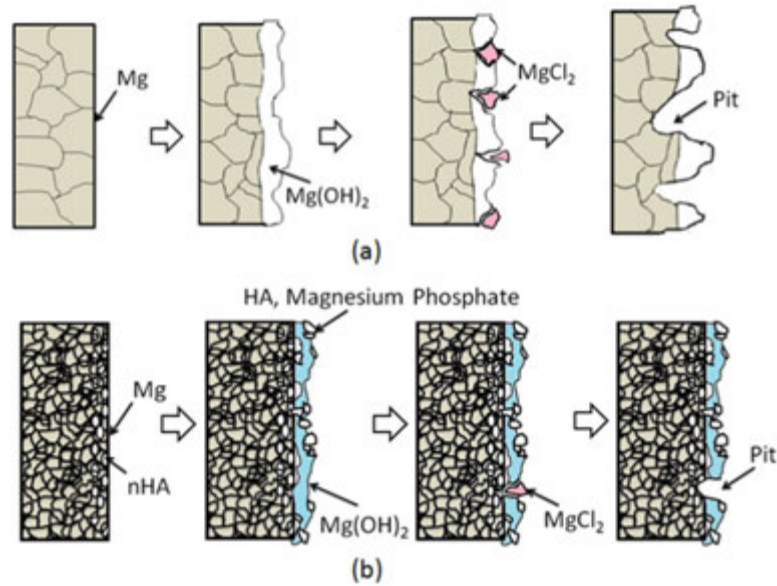


Fig. 6 Schematic illustration of effect of HA on enhancing corrosion resistance: (a) degradation mechanism in pure Mg and (b) degradation mechanism of Mg-HA composite. *Source:* Ratna Sunil, B., Kumar, A.A., Sampath Kumar, S.T., Chakkingal, U., 2013. Role of biomineralization on the degradation of fine grained AZ31 magnesium alloy processed by groove pressing. *Materials Science and Engineering C* 33, 1607–1615.

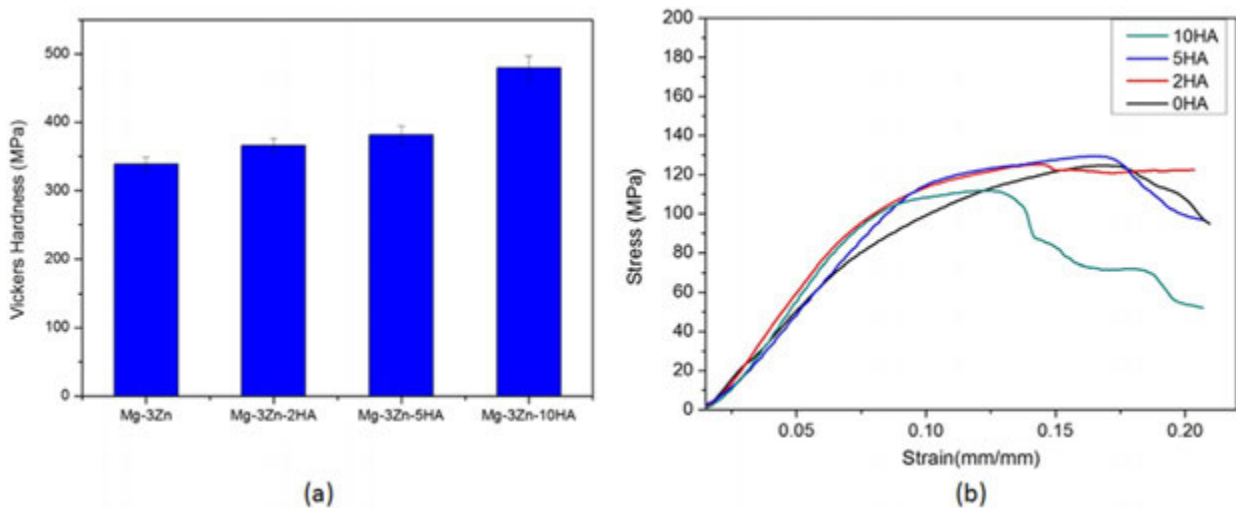


Fig. 7 Mechanical properties of Mg-3Zn-HA composites: (a) Average hardness and (b) stress-strain curves from uniaxial compression tests. *Source:* Jaiswal, S., Manoj Kumar, R., Gupta, P., *et al.*, 2018. Mechanical, corrosion and biocompatibility behaviour of Mg-3Zn-HA biodegradable composites for orthopaedic fixture accessories. *Journal of the Mechanical Behavior of Biomedical Materials* 78, 442–454.

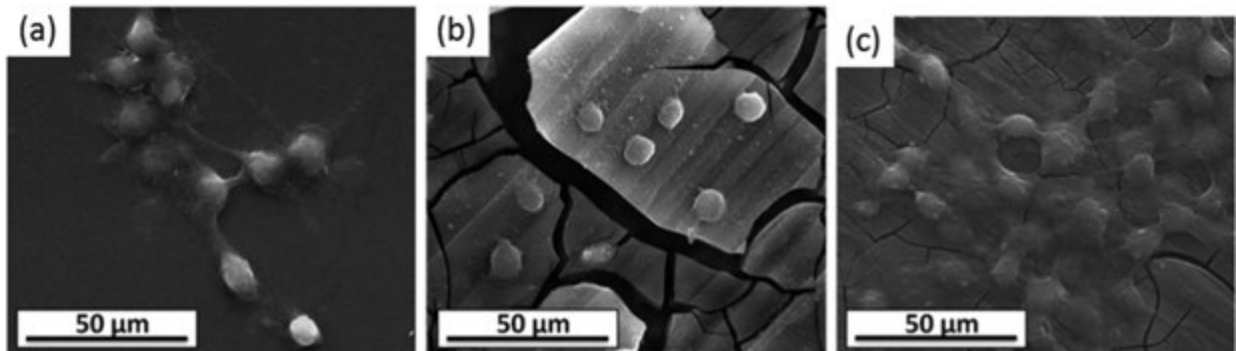


Fig. 8 Scanning electron microscope images of cell adhesion: (a) Standard tissue culture plate made of polystyrene, (b) pure Mg, (c) Mg-nano-HA composite. *Source:* Ratna Sunil, B., Sampath Kumar, T.S., Chakkingal, U., Nandakumar, V., Doble, M., 2014. Friction stir processing of magnesium-nanohydroxyapatite composites with controlled in vitro degradation behavior. *Materials Science and Engineering C* 39, 315–324.

effect on increasing the wettability of Mg as observed from the contact angle measurements by using water as solvent (Ratna Sunil *et al.*, 2014c). Further, higher mineral phases composed of HA and magnesium phosphate are formed on the Mg–HA composite. Nano-HA that present in the composite acts as nucleus and accelerates the deposition of mineral phases from the physiological solution. These mineral phases act as a coating and delay the degradation process. Presence of HA not only improves the biomineralization, but doing so, enhances the tissue response as typically observed from the scanning electron microscope (SEM) image of Mg–HA composite surface incubated with rat skeletal muscle cells (L6) as shown in Fig. 8. Compared with base material, Mg alloy with nano-HA has excellent cell response and adhesion.

Conclusions and Future Perspectives

Developing composites by combining multi-phases helps to impart different properties to the structures. For biomedical applications, all metals which are used to manufacture orthopedic implants are bioinert in nature. Bioactivity of these metals can be increased by providing bioactive polymer or ceramic coatings on the surface. On the other hand, materials which exhibit bioactivity can be embedded with the metals in bulk and by doing so, bioinert implants can be transformed as bioactive metals. This phenomenon is also applicable in developing Mg-based degradable biomaterials. Selection of type of reinforcement, size, shape, and level of distribution is crucial in developing Mg-based composites as the corrosion and mechanical properties are governed by these factors. Controlling the degradation rate in the physiological environment, without deteriorating the mechanical performance is the prime objective behind selecting any secondary phase while developing Mg-based composites. Additionally, selection of the reinforcement can be made by validating its efficacy to introduce more bioactivity, higher biomineralization to promote healing rate. In this context, ceramic materials which belong to the group of calcium phosphate mineral phases such as hydroxyapatite or tricalcium phosphate can be the optimum choice. When it comes to size of the reinforcements, nano-sized powder is preferable due to the demonstrated superior mechanical and corrosion properties.

Among all the available processing routes, powder metallurgy and friction stir processing routes have shown with lower number of complexities compared with the liquid state methods. Basically, being a highly reactive metal, Mg is unstable in the liquid state and readily forms oxides or intermetallics. Development of large grains in the composites is another limitation with the casting methods that results inferior mechanical performance. Powder metallurgy results pours structures with relatively improved level of distribution if proper blending procedure is carried out. However, porous structures are recommended for biomedical applications and hence, composites developed from powder metallurgy route offer additional advantage. Limitation with the size and shape of the implant that can be manufactured by powder metallurgy is the important concern in selecting this processing route to develop the composites. However, with the advent of modern manufacturing processes such as additive manufacturing techniques several issues are addressed in developing complex shaped implants using powder metallurgy. FSP is another promising route which facilitates to develop Mg-based surface composites within the solid state. However, the thickness of the surface composite that is produced by FSP is limited to a few millimeters. Implant tissue interactions are usually initiated at the surface. To functionalize the surface by incorporating bioactive ceramics into the surface, FSP is appropriate method. Additionally, combining multiple processes such as casting followed by FSP brings more advantages to develop Mg-based composites with improved bulk behavior along with enhanced surface properties. At present, no commercially available Mg based implants are seen in the medical applications. The status of the research is at the level of developing potential Mg-based composites and evaluating their in vitro and in vivo performance. More clinical studies are yet to be conducted and hopefully in the very near future, Mg-based degradable composites will occupy a prominent place in the medical industry for temporary implant applications.

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Metal Matrix Composite Syntactic Foams for Light-Weight Structural Materials

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Nomenclature

S (GPa) Structural stiffness

t (s) Time

W (J cm⁻³) Absorbed mechanical energy

ε (–) Engineering deformation

ρ_{rel} (–) Relative density

σ_{C} (MPa) Compressive engineering strength

σ_{CD} (MPa) Dynamic compressive engineering strength

σ_{Pl} (MPa) Engineering plateau strength

Abbreviations

CT computer tomography

LOM light optical microscopy.

MMCSF metal matrix composite syntactic foams

SEM scanning electron microscopy

TEM transmission electron microscopy

vol% volume fraction in percentages

Glossary

Effective elastic modulus The Young's modulus of a fictive body, substituting the investigated foam.

Interface layer A transition zone between the filler particles and the matrix material, ensuring the proper connection and load transfer between them. It can be either adhesive, cohesive, or mixed.

Relative density The density of the foam divided by the density of the foam materials in bulk.

Structural stiffness The slope of the initial linear part of the engineering stress–engineering strain curve and during which some plastic deformation may occur.

Introduction

Metal matrix composite syntactic foams (MMCSFs) are light-weight materials from the particulate reinforced metal matrix composites (MMCs) family. The filler particles in these materials are hollow inclusions such as hollow spheres, made of ceramics, metallic, or amorphous (glassy) materials. Fillers can be other particles with inner porosity, such as expanded perlite, clay or glass pearls, and fly-ash. Due to their inherent porosity, MMCSFs can be sorted into the metallic foams group as well. In this aspect, MMCSFs are amongst the high performance “heavier” foams with the typical relative density of 0.5 or higher. Theoretically, the matrix material of MMCSFs can be any kind of metal. Practically, light-weight materials are used in order to produce the lowest density MMCSFs as possible. The most commonly used matrix materials inevitably come from the Al alloys group (secondly from the Mg alloys). Besides conventional light-weight materials Zn, Ti, Fe, Cu, and other foams can be found in the literature as it will be detailed in this article.

The production methods of MMCSFs are under development. In the early techniques, stir casting was the prominent method, since it is simple and cheap. The disadvantage is in the lower volume fraction of the filler particles. Subsequently, gravity casting (and its counter version) and later liquid state pressure infiltration were more and more frequently applied, as it has the capability to produce higher volume fraction (higher porosity) MMCSFs, but disadvantageous in the costs point of view (more complex molds, more sophisticated equipment). Besides, powder metallurgy methods are spreading in the scientific community interested in the field of MMCSFs, due to its applicability to produce more complex materials and to join materials that may have extensive chemical reactions between the matrix and the filler particles. By increasing the magnification of the insight, the structure of the interface layers in the MMCSFs is revealed. This part focuses on the interface layer between the filler particles and the matrix that can be cohesive or adhesive in nature (in reality both). Since the task of this interface layer is to establish a firm connection and load transfer between the constituents, its properties and features are more than important.

After the production methods, the resultant structure is described in section “Structure of MMCSFs.” The macrostructure can differ according to the production method and can also be different due to the different applied filler grades. Simple MMCSFs are produced by using unimodal hollow particles (most commonly hollow spheres). But the possibilities are significantly more broad. For example, bimodal spheres can be applied or the fillers can be made from different materials. These MMCSFs are called hybrid MMCSFs and may present unique mechanical properties.

The MMCSFs are most promising in the light-weight structural applications since their low density and high specific properties. Therefore, section “Mechanical Properties” is dealing with the mechanical properties of MMCSFs. The main load mode of foamed materials is compression. Since MMCSFs are relatively new materials, only the measurement methods and circumstances of quasi-static compression are summarized in an international standard (ISO, 2011). The larger density of MMCSFs (compared to “conventional” metallic foams) is connected to extremely high (specific) compressive strength compared to other, less advanced metallic foams (in some cases the compressive strength can be higher than 200 MPa) and high energy absorption capability as well during the plastic deformation or failure of the samples. The strength, stiffness, and energy absorption capability can be further improved by solid outer shells in the case of laminates or filled sections. These properties predestinate MMCSFs as ideal materials for structural application in which the load are low or moderate, but the light weight is extremely important. Moreover, MMCSFs are often aimed to be used as collision dampers or as protective materials against projectiles (such as conventional metallic foams) in defensive applications (mainly vehicle armors can be considered here). In these cases, the dynamic properties of foams, especially the energy absorption capability and the failure mode, are extremely important. These properties have been tested by pressure bars (for example split-Hopkinson pressure bars) or by directly fired projectiles. The former is capable to produce objective measures, while the latter is more practical and grants qualitative insight. Based on the results, the strain rate sensitivity of the MMCSFs can be determined. Besides quasi-static and high strain rate loads, the repetitive loading of the MMCSFs is important in the case of structural applications at least subjected to compressive cyclic loads. By the corresponding tests, the lifetime region and the fatigue limit of the materials can be determined based on the conventional fatigue tests, evaluated by statistical methods (Gauss-, or Weibull distribution) and by the stair-case method, respectively. On this basis, the Wöhler-curve (or S–N curve) of MMCSFs can be constructed along with the observations on the failure mechanisms of the samples. The mechanical characterization of a material cannot be complete without the investigation of the stress concentration and the notch sensitivity of the MMCSFs. These properties are important when these heterogeneous in nature of materials are in the form of parts with a given geometry carrying geometrical inhomogeneities (such as fillets, keyways, holes, etc.). The related properties are the fractures energies (the mechanical energies absorbed up to the failure of the MMCSFs samples or parts) and the toughness of the material (similar to the fracture toughness of bulk materials, but interpreted for the porous structures). The samples and the measurement techniques of these mechanical properties, especially the fracture toughness, are more sophisticated and complicated, therefore the available literature on these properties are relatively limited.

In the hope of the author, the introduction and discussion of the above-mentioned features and properties are helpful to situate the MMCSFs amongst the conventional foams and dense materials.

Materials for MMCSFs

Regarding the constituents of MMCSFs, basically, two materials should be chosen: (1) one for the matrix and (2) one for providing the porosity. Afterward, the latter is referred as “filler material” (in the nomenclature of metal matrix composites, these should be called “reinforcing particles” or something similar, but in MMCSFs the strengthening – at least in general and in absolute value – is not a necessary requirement).

Matrix Materials

As the original point of the foams’ application was the weight reduction (connected to the increment of mechanical strength) light-weight alloys are the most common matrix materials for MMCSFs. Besides these alloys, for special purposes, Ti-, Zn-, Fe-, and Cu-based MMCSFs can also be found in the literature.

The literature is overwhelmed by Al alloys as they are cheap, easily available, and easy to handle, especially in the case of liquid state production (see next section). Amongst Al alloys, technical purity Al and Si alloyed Al are the most common, extended by some Mg addition. The pure Al (Dou *et al.*, 2007; Wu *et al.*, 2007; Lin *et al.*, 2016a, 2017) is explained by the purely scientific approach: The trends and phenomena caused by the variation of the fillers (their material, spatial distribution, volume fraction – connected to the porosity) is not affected by the alloying elements, the measured properties, and features depends only on the macro- and microstructure and the fillers; therefore, they can be considered as matrix independent. Moreover, the comparability of the differently composed MMCSFs is easier as well. The Si addition is justified by practical considerations: Si alloying in Al decreases the melting point of the alloy (the binary Al–Si alloy, containing 12.8 wt% Si has as a low melting temperature as 575°C) and also decrease its viscosity of the melt; consequently, the handling of the molten alloy during a liquid state production method is easier, the filling of the mold is better and the infiltration is also easier and more complete (Rohatgi and Guo, 1997; Ramachandra and Radhakrishna, 2005). The Mg addition (Zhang *et al.*, 2018) has two major rules: (1) on one hand it, “improves” the wettability (the contact angle is decreased) and (2) on the other hand with additional Si alloying the alloy becomes precipitation hardenable (Zetl *et al.*, 2001; Lin *et al.*, 2016a,b). More complex, high-performance Al alloys, such as Cu (Sahu *et al.*, 2019) and Zn–Mg (Balch *et al.*, 2005; Balch and Dunand, 2006) alloyed compositions can also be found in the literature.

The next and very promising generation of MMCSFs is produced by Mg-based alloys. Example of pure magnesium matrix (Nguyen *et al.*, 2016) can be found in the literature, but in most cases, Al and Zn alloying are the most common. The production of these kinds of MMCSFs is more complex: because of the high reaction affinity of Mg with O, additional safety precautions and

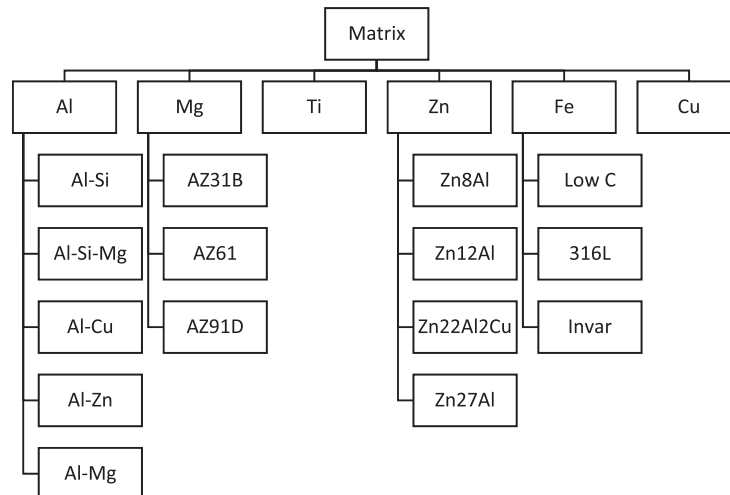


Fig. 1 Typical matrix materials for MMCSFs.

instructions are required. Basically, three grades are used: AZ31B (Xia *et al.*, 2018), AZ61 (Akinwekomi, 2019) and AZ91D (Rohatgi *et al.*, 2009; Huang *et al.*, 2011; Anantharaman *et al.*, 2015; Anbuechhiyan *et al.*, 2017; Braszczyńska-Malik and Kamieniak, 2017a,b; Anbuechhiyan *et al.*, 2018).

Considering the density of the possible matrix materials, the next in the row is the Ti. The application of Ti as the matrix of MMCSFs has been inspired by medical ideas to replace human bone tissues in the form of metallic foams. In the literature pure Ti (Xue and Zhao, 2011; Mondal *et al.*, 2012; Xue *et al.*, 2012; Jha *et al.*, 2014; Mandal *et al.*, 2015) can be found as the matrix material of cenosphere filled MMCSFs. Due to the high cost and hard handling of Ti, powder metallurgical routes (see later) are the most common ways to produce this kind of MMCSFs.

Rarely, Zn alloys have also been applied as matrix material. Zn8Al (Pan *et al.*, 2018; Mohbe *et al.*, 2019), ZnAl12 (Daoud, 2009), Zn22Al2Cu (Daoud, 2008; Aragon-Lezama *et al.*, 2015; Sánchez-Martínez *et al.*, 2016) and Zn27Al ~25 wt% Al alloyed (Linul *et al.*, 2018; Manoj *et al.*, 2018; Movahedi *et al.*, 2019), due to its high damping capacity, good mechanical properties, connected to good castability, low melting point and corrosion resistance. Since ~50% of density reduction can be reached by the application of hollow inclusions, these MMCSFs can be interesting in applications, such as engineering applications in the transportation and construction industries. An additional advantage is in the solution heat treatment and aging of these alloys, granting higher mechanical properties and toughness.

As one of the most common structural material in engineering practice is iron (Peroni *et al.*, 2012a,b) and steel (mainly the austenitic corrosion resistant grade of 316L) (Vendra *et al.*, 2009; Castro and Nutt, 2012a,b; Rabiei and Garcia-Avila, 2013; Peroni *et al.*, 2014; Weise *et al.*, 2014), these materials are also tried as a matrix material of MMCSFs. Due to their mechanical properties, the iron and steel-based MMCSFs are more than prospective; however, due to their high melting point and strong affinity towards the chemical reactions with the fillers materials makes the production of these materials hard. A superalloy (Invar) with 36 wt% of Ni has been also applied to produce MMCSFs (Weise *et al.*, 2013; Luong *et al.*, 2015). The idea behind this matrix in its low coefficient of thermal expansion, that is closer to the coefficient of the filler material and therefore is better to produce MMCSFs with less inner stresses.

The last matrix material that is mentioned in the literature (at least in theory) is Cu (Pérez *et al.*, 2018). This matrix can be advantageous in the case of thermal applications, where high heat conductivity is required, but may have too high density. The typical matrix materials are summarized in Fig. 1.

Filler Materials

According to the original idea of polymer matrix composite syntactic foams, the filler material is a set of hollow spherical inclusion. In the case of a metallic matrix, the situation is a little more complex, since in MMCSFs the load is significantly higher. The filler materials can be sorted into two main groups: Hollow shells and porous particles. The main requirements for the fillers for MMCSFs are: (1) To have closed, continuous surface, (2) to be porous, (3) to be light and (4) to be resistant against the conditions during the production (chemical reactions, heat, pressure, high temperature).

The first filler materials were cheap fly-ash particles (Zhang *et al.*, 2009; Huang *et al.*, 2010, 2011; Braszczyńska-Malik and Kamieniak, 2017a,b,c; Akinwekomi, 2019) originating from the combustion process in thermal power plants and separated from the ash by a cyclotron. These particles are more or less spherical and can be described as hollow spheres. The average diameter of the spheres is in the range of a few hundred microns, with a typical wall thickness of one-tenth of the diameter. The wall of the hollow spheres often has inner porosity. The chemical composition of the fly-ash particles depends on the fuel (and on its actual quality) burned in the power plant. Basically, they are built up from mixed oxides, containing silica (~70–80 wt%), alumina

(~20–30 wt%) and other oxides (Na, Ca, K). Due to their various chemical composition and wall porosity, their mechanical properties are uncertain and show high scatter.

Still connected to the polymer matrix composite syntactic foams, the next commonly spread filler particles were glass hollow spheres (Peroni *et al.*, 2012a; Lehmhus *et al.*, 2014; Panteghini and Bardella, 2015; Lin *et al.*, 2016b; Anbuezhhiyan *et al.*, 2018; Zhang *et al.*, 2018; Lin *et al.*, 2019). The chemical composition of glass microballoons is more controlled, the production method is more sophisticated and therefore the size range and the mechanical properties of the filler particles have lower scatter, therefore the properties of the MMCSFs themselves are more predictable. Besides this, their advantage is in their low cost. The disadvantage of glass hollow spheres is in their chemical composition since they are consisting of ~70%–90% SiO₂ and remaining various oxides and due to this, they are quite sensitive to chemical reactions with the matrix materials. Therefore, attempts have been made to coat the glass hollow spheres to make them more resistant against molten Mg for example (Lin *et al.*, 2019). Coatings are also used to improve the wettability conditions between the phases (fly-ash filler and molten metal, in the case of liquid state production methods) (Braszczyńska-Malik and Kamieniak, 2017a,c).

By the evolution of MMCSFs, the demand for fillers with higher mechanical properties and better resistance against molten metals increased ever and ever. This lead to the production and application of ceramic hollow spheres. Due to its availability, relatively low cost and easy handling, alumina (Al₂O₃) is the most common and widely used (Ferguson *et al.*, 2013; Santa Maria *et al.*, 2013, 2014; Omar *et al.*, 2015; Su *et al.*, 2018). Thanks to the advantageous properties of Al₂O₃, the MMCSFs filled by them show extreme compressive properties, especially compressive strength, but also exhibit brittleness (Ferguson *et al.*, 2013; Santa Maria *et al.*, 2013; Su *et al.*, 2018). To further increase the performance of MMCSFs SiC (Luong *et al.*, 2013; Cox *et al.*, 2014) was also proposed for the material of hollow spheres. Besides their outstanding mechanical properties, this approach resulted in extremely low density, regarding at least the family of MMCSFs. Researches in the field could decrease the density as low as 1 g cm⁻³ by Mg matrix (Anantharaman *et al.*, 2015). The disadvantage of these high-performance hollow inclusions is in their high costs. Their production needs carefully planned protocols and rigorous conditions (chemical composition, temperature, pressure, etc).

The need for low density, high performance, and cheap MMCSFs is increasing. Therefore, new filler materials have been searched and tried, recently. The main difference of these fillers can be found in their inner structure, since they are not completely hollow, but have a porous (foam-like) inner structure, usually with irregular shape and size inner pores. Due to the irregularities of the inner structure, the mechanical properties exhibit larger scatters. These fillers offer the possibility to produce low-cost MMCSFs with moderate mechanical properties in large volumes. One of the most common is expanded perlite (Taherishargh *et al.*, 2014a,b, 2018; Fiedler *et al.*, 2015a,b; Taherishargh *et al.*, 2015b; Broxtermann *et al.*, 2017; Taherishargh *et al.*, 2017b), studied by the research group of Fiedler. The studies included basic mechanical properties as well as the behavior of the material at elevated temperatures or at higher strain rates. Another approach was to apply pumice as filler material, that is a low-cost natural porous volcanic glass with tubular pores. The tubular pores caused higher strength values in the direction of the tubular pores axes (Taherishargh *et al.*, 2015a). Similar material is expanded clay available with various chemical compositions and in various sizes (Bazzaz Bonabi *et al.*, 2014; Puga *et al.*, 2018). The production of MMCSFs with expanded clay particles was found to have a homogeneous structure, more or less equal pore structure, and isotropic properties. The MMCSFs can be advantageous as low-cost and light-weight casted structural components in the future. Last, but not least expanded glass is also an option as filler material of MMCSFs (Al-Sahlani *et al.*, 2017; Wright and Kennedy, 2017). The problems with this filler are the different thermal expansion and the reactivity with the matrix material. The advantages are in the density (the produced MMCSFs were around 1 g cm⁻³) and in the low cost. The filler materials are summarized in Fig. 2.

Interface Layer

The third important part of a particle-filled MMCs is the interface layer between the particles and the matrix material, responsible for the load transfer from the matrix to the particles, that is an important and determinative role in the composite. The interface layer can be two in nature: (1) Cohesive or (2) adhesive. In practice their mixture is typical. The cohesive connection originates from the chemical reactions between the matrix and the filler. In this aspect, the fillers can be inert (such as Al₂O₃ hollow spheres in aluminum) or reactive (for example SiO₂ in aluminum). The most common chemical reactions in usual MMCSFs with ceramic fillers that contain reactive components are the following:



In these cases, the molten metal reacts with the active component of the fillers' material. This can be advantageous because can result in a better (stronger) connection between the filler and the matrix. On the other hand, the reaction can be disadvantageous, since the reactions can harm the wall of the fillers (dissolve them) and this can result in lower mechanical properties. In the case of Al-based MMCSFs with Al matrix, the following reactions may occur:



In this case, the molten metal reacts with the metallic hollow sphere. This results in the solution of Fe into Al and forms need like precipitations, that may increase the brittleness.

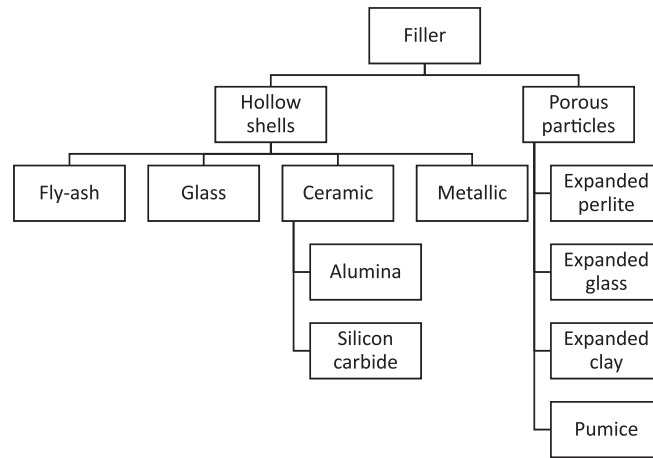


Fig. 2 Typical filler materials for MMCSFs.

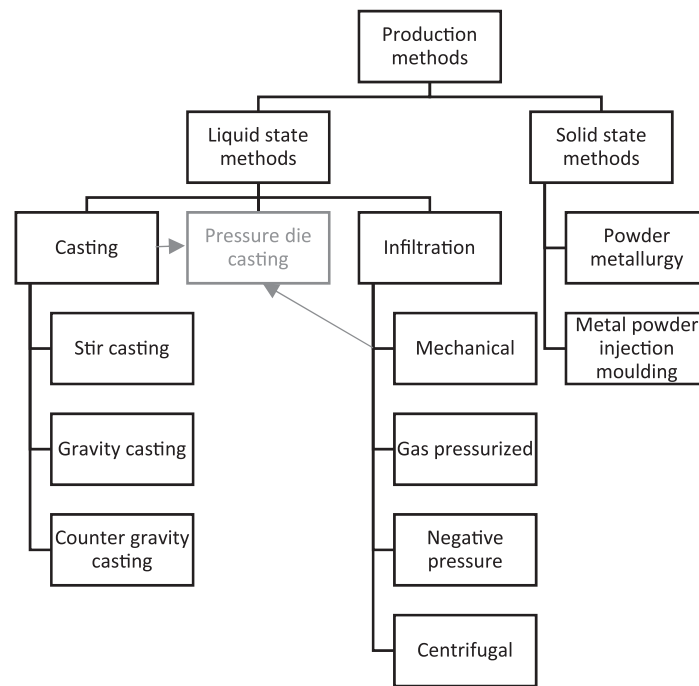


Fig. 3 Most common production methods of MMCSFs.

In summary, the reactions between the constituents of the MMCSFs can be advantageous, when resulting in better connections and therefore better load transfer.

Production Methods

The MMCSFs can be produced by following different routes and approaches. Basically, the production methods can be divided into two groups: (1) Liquid state methods and (2) Solid-state methods. The basic routes are shown in Fig. 3.

Considering the liquid state methods, the first and simplest basic method is casting. The first approach to produce was the stir casting method, often applied to produce particle reinforced MMCs. In the first step of stir casting, the matrix alloy is melted (usually under the protection of salt or inert gas) and typically overheated, then during the continuous stirring of the melt the filler particles are added. After the homogenization of the mixture, the system is let to cool down and solidify. The method is simple (at least in the case of relatively low melting point materials), cheap and easy to use. Its main disadvantage is in the limited volume

fraction of the filler (since they are increasing the viscosity significantly and due to the stirring they may break). Due to its simplicity, the method has been used for Al alloys (Rajan *et al.*, 2007; Mondal *et al.*, 2009, 2018) and Zn alloys (Daoud, 2008; Manoj *et al.*, 2018) as well.

The next method to be considered is gravity casting (Vendra and Rabiei, 2007; Castro and Nutt, 2012a; Bazzaz Bonabi *et al.*, 2014). In this case, the filler particles are poured into a (metallic) mold and usually densified by rigorous tapping or vibration. The set of the fillers is often tied down by a steel mesh to prevent the floating of the hollow filler particles. After the preparations, the previously molten metal is poured on the fillers and flows into the empty space between the particles. This method works only in the case of low wetting angles between the material of the filler and the molten metal and if the capillary effects can be neglected (relatively large filler particles).

Later, the method was modified to help the exhaust of the gases (air) from between the filler particles (Rabiei and O'Neill, 2005). The method is well known in the casting industry as counter gravity casting. The required conditions (low wetting angle, relatively large particles) are the same, but the molten metal enters from the bottom of the prepared mold. In this case, the gases between the particles can leave the system upwards and in this way, the MMCSFs will contain less unwanted porosities (a pore is considered unwanted if it does not result from the hollow fillers).

The next main group in the series of production methods is the infiltration when additional pressure is applied to help the infiltration of the molten metal among the hollow fillers. The additional pressure may originate from mechanical forces applied through plunges or other metallic parts (Zhang and Zhao, 2007; Castro and Nutt, 2012b; Taherishargh *et al.*, 2014a,b, 2015b, 2018; Fiedler *et al.*, 2015a; Sulong *et al.*, 2015; Taherishargh *et al.*, 2015a, 2017a; Borovinšek *et al.*, 2016; Broxtermann *et al.*, 2017; Taherishargh *et al.*, 2017b). In other cases, the required additional pressure to overwhelm the forces acting against the infiltration was ensured by an inert gas (typically argon or nitrogen). The molten metal solidifies under pressure in these methods, therefore the amount the so-called unwanted porosity (the porosity originating not from the filler and usually located between the filler particles around their contact points) is significantly lower and the properties of the produced MMCSFs are better. In the cases of both infiltration techniques, the volume fraction can be higher, compared to the stir cast method and can reach ~64 vol% in the case of spherical filler particles with identical diameters (Jaeger and Nagel, 1992; Torquato *et al.*, 2000). Even higher filler volume fraction can be provided through the application of filler particles sets with bimodal or multimodal size (diameter) distribution (Brouwers, 2006). Regardless of the applied method, the main parameters of the infiltration are (1) the infiltration temperature, (2) the infiltration pressure and (3) the infiltration time. These parameters have determinative effect on the quality of the MMCSFs and on the infiltrated length, in other words on the maximal producible size (Rohatgi *et al.*, 1998, 2006a,b; Palmer *et al.*, 2007; Dobránszky *et al.*, 2008; Orbulov and Dobránszky, 2008; Orbulov, 2011; Ginsztler *et al.*, 2013). The infiltration temperature is more or less determined by the melting point of the matrix material, moreover, some overheating is required, since the infiltrating metal should be in liquid state until the end of the process to prevent the freezing of the melt front, that would result in poor or incomplete infiltration. On the other hand, too high overheating should be avoided, because the alloying elements can burn out and the disadvantageous chemical reactions detailed in the previous subsection are faster at a higher temperature. Regarding the infiltration pressure, the infiltrated length is a linear function of the infiltration pressure (Orbulov, 2011, 2013). The infiltration pressure is limited by the mechanical capabilities of the mold in which the MMCSF is produced and by the crush strength of the filler particles. If the pressure is too high in the aspect of the filler particles, they may crush and then, the produced material will not be a MMCSF, because, the molten metal infiltrates the broken filler particles. If the mold is the weaker point of the system, leakage may occur causing safety concerns. The infiltration time (the duration from the built-up of the infiltration pressure until the release of the pressure or the solidification of the matrix) has the most complex nature and effect on the infiltrated length. By theory, the infiltrated length is a square root function of time as it was derived by Kaptay and others (Garcia-Cordovilla *et al.*, 1999; Kaptay, 2008). However, mostly in the short infiltration time regions, measurements showed not square root, but exponential (continuously increasing slope instead of a decreasing one) nature (Muscat and Drew, 1994). This mismatch is interesting in the future, automated and large-scale production of MMCSFs, based on pressure die casting (please refer to the production method represented in dark gray in Fig. 3). This method has not been completely adopted for the production of MMCSFs, the main problems are the automated filling of the mold cavity, relatively low casting pressure (instead of the currently used high pressures to decrease the number of porosities in the cast parts) and the correct setting of the pressure casting parameters, similarly to the case of mechanical or gas pressure infiltration. Due to the latter aspect, the infiltrated length–infiltration time relationship in the short time domain is important and was investigated (Orbulov, 2013). By the rigorous and precise, high-frequency measurement of the infiltration time and infiltration pressure, the linear relationship between the infiltration length and the infiltration pressure and the square-root relationship between the infiltration length and infiltration time have been confirmed according to the available theoretical considerations.

The infiltration procedure can be “reversed,” by applying negative pressure on the other side of the system fulfilled by the filler particles, instead of applying a positive pressure on the molten matrix (Braszczyńska-Malik and Kamieniak, 2017b; Anbucheziyan *et al.*, 2018). By this method, the theoretical pressure difference that initiates the infiltration can be 1 bar maximum. Therefore, this method is applicable only if the required infiltration pressure is below this theoretical limit, in other words, the wetting angle is at least not far from 90°.

Naturally, other infiltration procedures can be imagined, for example, an interesting solution is the application of centrifugal forces to infiltrate the molten metal into the pack of filler particles (Sánchez-Martínez *et al.*, 2016). In this case, the size of the sample can be a limit since larger samples have a larger moment of inertia and require higher energy to rotate them at the desired revolution.

Besides the liquid state methods, a few solid state procedures are also available. The first, that has to be mentioned here is the powder metallurgy. Generally, the method is based on the mixture of a fine powder, their compaction at relatively high pressures and the sintering of the compacted parts at high temperatures (usually above the recrystallization temperature of the matrix material). In the case of the MMCSFs, the production steps are extended by the introduction of the filler particles into the matrix powder. The advantages of the powder metallurgy are: (1) It is applicable in the case of special, not so easy to handle materials for example for Ti, that is extremely sensitive to the presence of gases at high temperature (Xue and Zhao, 2011; Mondal *et al.*, 2012; Xue *et al.*, 2012; Jha *et al.*, 2014; Mandal *et al.*, 2015), or heavily alloyed austenitic corrosion-resistant steels (Neville and Rabiei, 2008; Hu *et al.*, 2018) or pure matrices such as pure Fe (Neville and Rabiei, 2008) and pure Al (Vogiatzis *et al.*, 2015; Vogiatzis and Skolianos, 2016); (2) the intensity of the chemical reaction between the fillers and the matrix is lower, due to the lower process temperatures; (3) unique mixtures of matrix materials (even if the components are not alloying) can be produced. The process has disadvantages as well: (1) Due to the crush strength of the fillers, the compaction pressure is limited, the porosity in the matrix can be relatively high; (2) it is an expensive method and requires larger investment (the powders are expensive, special equipment is needed).

The last, but relatively new production method in solid-state is the injection molding, initially suggested by Weise *et al.* for Invar (Weise *et al.*, 2013) and for 316L (Weise *et al.*, 2014) matrices. In this case, the matrix powder is mixed with the fillers and a carrier material, usually some kind of polymer. Then, the mixture is injected into a mold on a “conventional” injection molding machine. The injected parts are removed from the mold as “green parts,” then they are heat treated to remove the binder (carrier) material to get “brown parts.” The brown parts are further heat treated, usually in a two-stage process (Yu and Qian, 2012). The porosity, shape, and size of the samples are strongly depending (1) on the injection molding parameters, (2) on the matrix materials, and (3) on the parameters of the heat treatments.

In summary, the possibilities for MMCSFs production are quite wide, all of the processes have their advantages and disadvantages. The best solution is always depending on the composition of the required MMCSFs and on the possibilities for the investments. In the future, pressure die casting is a promising method for the large scale, mass production of relatively small parts.

Structure of MMCSFs

The structure of the MMCSFs can be discussed at different magnification levels and correspondingly the macro- and the micro-structure can be revealed. In this section, the author writes about “structure” in general, since the border between the two different approaches is not sharp in the case of MMCSFs.

The structure of the MMCSFs can be investigated by destructive and nondestructive methods. In the case of the destructive methods, a section of the MMCSFs is investigated usually starting at lower magnifications by light optical microscopes (LOM) and approaching to more sophisticated details at high magnifications in scanning electron microscopes (SEM) or in transmission electron microscopes (TEM). The former is very common in the literature and almost applied in every case to reveal the interface layers between the components, while the latter can be said very rare, since the difficulties of the sample preparation, that is not easy in the case of bulk materials and even harder in the case of such porous materials as MMCSFs. On the nondestructive side, the computer tomographic (CT) methods (Kozma *et al.*, 2015) are common even in the case of “in situ” mechanical investigations (Adrien *et al.*, 2007; Lachambre *et al.*, 2013). The scanned structures are used to build the material in a virtual environment and to perform finite element investigations on the structure to obtain material laws for the further studies of the MMCSF parts (Maire *et al.*, 2003; Kozma *et al.*, 2014, 2015).

The structure of MMCSFs can be very different. In this point of view, based on the diameter distribution of the filler particles, the author distinguish unimodal, bimodal (Tao *et al.*, 2009; Orbulov *et al.*, 2019), moreover multimodal MMCSFs (as shown in Fig. 4). In the case of unimodal MMCSFs the size of the hollow spheres follows a relatively narrow Gaussian-distribution, while in the case of bimodal distribution, the situation is similar, but there are two (perhaps overlapping) Gaussian distributions. By setting the amounts of the different sized fillers, the density and the mechanical properties of the MMCSFs can be tailored for the specific requirements of the designed components. Filler particles, with more than two peaks in the size distribution curve, can be also imagined; however, there is no existing example in the literature according to the best knowledge of the author.

Besides the classic MMCSFs hybrid versions can be designed and produced by (1) applying different material filler particles (Májlinger and Orbulov, 2014; Májlinger, 2015; Orbulov and Májlinger, 2015; Májlinger *et al.*, 2016a,b) or (2) by applying additive materials such as reinforcing particles or fibers (either long or short) in the matrix material. In Fig. 5(a) MMCSF filled by ceramic and metallic hollow spheres is represented as an example for the first case. These structures are interesting since they are joining the properties of high crush strength, but rigid and brittle ceramic hollow spheres and the ductility and deformation capability of the metallic hollow spheres. By the different ratio mixtures of the ceramic and the metallic hollow spheres, the mechanical properties can be set (Májlinger and Orbulov, 2014) and not only the strength values as in the case of the bimodal (and multimodal) MMCSFs but the ductility, the structural stiffness, and the absorbed energies as well. Moreover, most of these properties can be estimated by the simple rule of mixtures but considering only the properties of the matrix material and the properties of the ceramic hollow spheres.

In the case of the application of additive materials, the aim is most commonly to increase the strength of the MMCSFs in general or in a given direction. These efforts usually cause the increment of the density as well. An elegant and possibly high performance, real-life example for the unidirectionally reinforced version are the low weight I-beams. The simple version that is shown in Fig. 6(a) was developed and manufactured by the research group of the author.

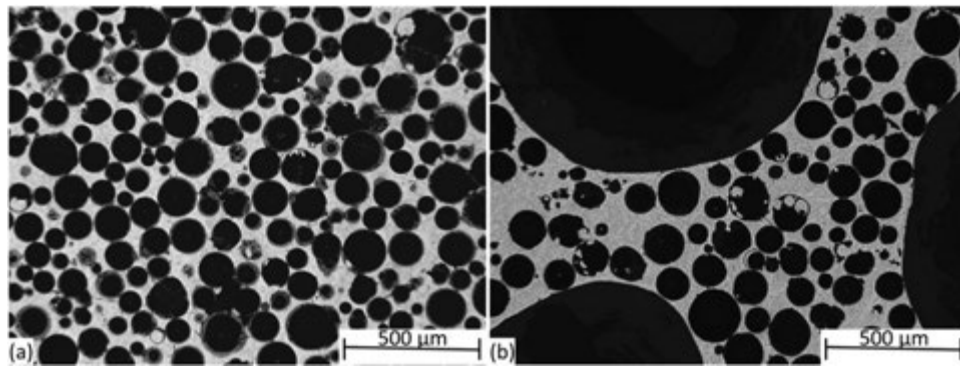


Fig. 4 MMCSFs with (a) unimodal and (b) bimodal structure.

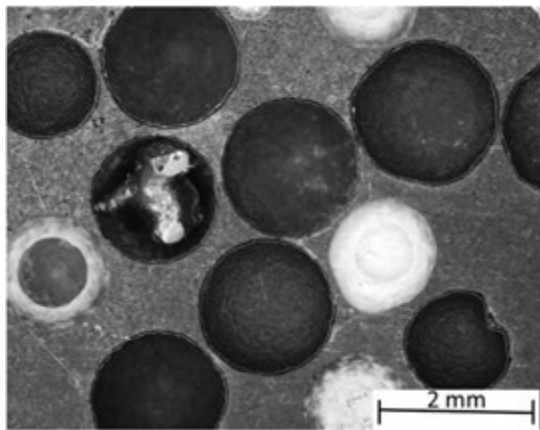


Fig. 5 MMCSF with 80 vol% metallic and 20 vol% ceramic hollow sphere filled hybrid structure.

The matrix of this special I-beam developed for extremely light (as low density as $\sim 1.5 \text{ g cm}^{-3}$), moderate load structural components is an MMCSF with AlSi12 matrix filled by $\sim 65 \text{ vol\%}$ mixed oxide ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) ceramic hollow spheres. The hollow spheres can be clearly observed in the lower half of **Fig. 6(b)** (as dark circles) and in the bottom-left corner of the SEM images in **Fig. 6(c)** and **Fig. 6(d)**. This low-density structure has been reinforced in the load-bearing parts (flanges) by the series of composite wires, having AlSi12 matrix and $\sim 60 \text{ vol\%}$ mixed oxide ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) long fiber reinforcement (Blucher *et al.*, 2001, 2004). The composite wires have high tensile strength, therefore ideal for reinforcing the structure. The cross-section of the composite wire can be observed in the upper half of **Fig. 6(b)**. Every small, dark dot is the cross-section of a mixed oxide ceramic fiber, with an average diameter of $\sim 12 \mu\text{m}$ (note: this type of fiber typically has elliptical cross-section). In the SEM images, the region between the foam matrix and the composite wire can be also observed. The interface region is smooth and continuous, the infiltration of the fillers in the matrix and in the reinforcement wires can be considered excellent and good, with small discontinuities, respectively. In the SEM images about the fracture surfaces, the nature of the break is brittle in the case of ceramic components and ductile in the case of the Al alloy matrix. The special I-beam can have the same strength compared to the pure Al alloy made one; however, at the density level of $\sim 1.5 \text{ g cm}^{-3}$ instead of the $\sim 2.65 \text{ g cm}^{-3}$ density of the Al alloy.

Mechanical Properties

As for new materials, the determination of the mechanical properties of MMCSFs is extremely important, most of the publications in the professional literature deal with this task in different aspects. Therefore, and due to the page limitations of this section, this overview cannot be fully complete, but can give general references and trends regarding the most important properties of the MMCSFs.

As the main load type of foamed materials is compression, the quasi-static compressive test of the cellular materials has been standardized (ISO, 2011). None of the other testing methods or measurements have been investigated in such details and there are no existing standards further. Since the aim of this section is to give a general insight into the possibilities and capabilities of the MMCSFs, the quasi-static mechanical properties are presented by region plots based on measurements from world-wide research

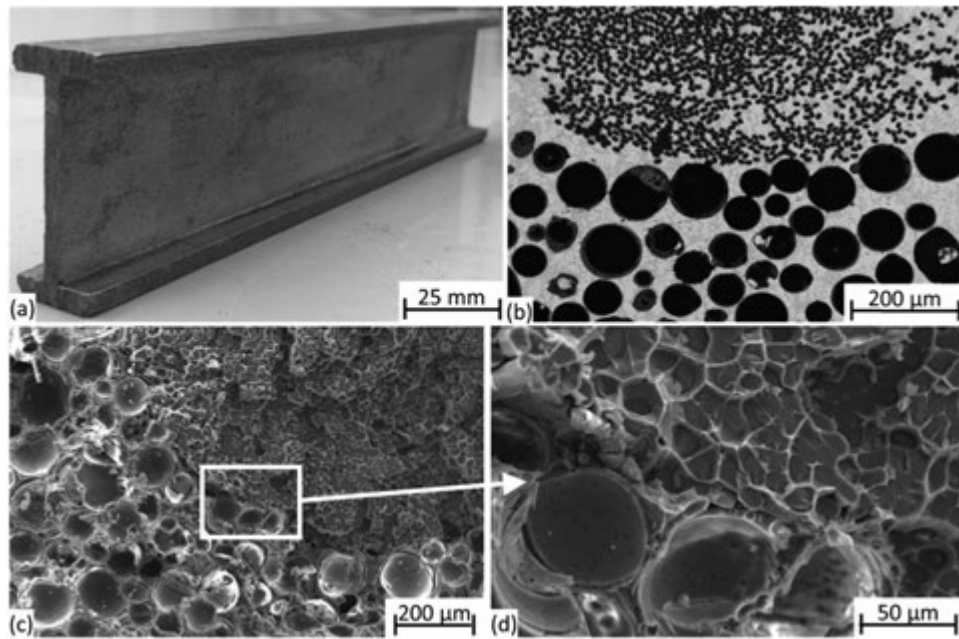


Fig. 6 Application of hybrid MMCSFs (a) macro photo of a lightweight I-beam; (b) LOM micrograph about the interface region between the foam matrix and the reinforcing wire; (c) and (d) SEM micrograph of the similar region.

groups (black markers) and the author's own research group (red markers) in the function of the foams' relative density. This way, the early works focus on the quasi-static properties of the MMCSFs with various compositions as it was described earlier. The most important properties in the quasi-static investigations are the compressive and the plateau strengths depicted in [Fig. 7\(a\)](#) and [Fig. 7\(b\)](#), respectively. The data were collected from the available literature referenced above; however, they were not differentiated, since the only investigated parameter, in this case, is the relative density of the MMCSFs. The compressive strength ([Fig. 7\(a\)](#)) is the measure of the initialization of the macroscopic permanent (either plastic or by cleavage) deformation. Therefore, it can be used as a limit value for design with a respective safety factor as it is common in conventional design process dealing with structural applications. The plateau strength is important in the energy absorption point of view as the length and the stress level of the plateau region are determinative parameters. The higher stress level and the longer plateau region result in larger absorbed mechanical energies during the deformation of the samples.

In both sub-figures of [Fig. 7](#), the existing results are highlighted by (1) yellow background in the case of MMCSFs and (2) red background for the case of the most common conventional metal foams. Besides, the green region is for the advanced versions of MMCSFs that are to be developed with reinforced (presumably particle and/or short fiber reinforcement) matrices. By analyzing the existing results, the strength values show an increasing trend with the relative density. The strength values of metallic foams are often described by power-law function; however, they are rarely used in the case of MMCSFs. As it can be seen in [Fig. 7](#), the ranges of the compressive and plateau strength values are similar, because the research groups usually aimed maximal energy-absorbing efficiency (that is the ratio of the actual absorbed energy, compared to an idealized foam, that has flat plateau region from the beginning of the deformation, up to a certain deformation limit). The energy absorption during the deformation of the foam is especially important in the applications of these materials. The absorbed energies from the literature against the relative density values are plotted in [Fig. 8](#) and color-coded as above.

The energy values are showing very similar trends to the plateau strength values, as the plateau strength is the main parameter that is effecting the energy absorption, besides the failure modes of course. The currently available energy absorption capacity is in the magnitude of $\sim 100 \text{ J cm}^{-3}$. The most dividing property of the MMCSFs is their stiffness. In many references, the slope of the initial linear part of the compressive engineering stress-strain curves is referred as Young's moduli of the foam (however, in the opinion of the Author it is not correct since the elastic (or Young's) modulus belongs to the bulk materials). According to the standard for compressive testing of foams the linear part is defined as the structural stiffness of the materials (and during this part some plastic deformation also occur (again, against the definition of the elastic or Young's modulus)) ([Kádár et al., 2016](#)). The structural stiffness values against the relative density values are plotted in [Fig. 9](#).

As it can be seen in [Fig. 9](#), there are a few outstanding stiffness values resulting from the above-detailed misunderstanding of the elastic modulus' definition and representing the real elastic modulus of the MMCSFs. However, these values are valid at very low load levels, therefore their significance in the application of MMCSFs are limited. Regarding the effective elastic modulus (the modulus of a fictive bulk material that can substitute the MMCSF itself) of the MMCSFs, it is an important task to determine it by measurements ([Szlancsik et al., 2017](#)) or by calculations ([Bardella and Genna, 2001a,b](#); [Bardella, 2003](#); [Marur, 2004, 2005, 2009, 2010](#); [Bardella et al., 2012](#); [Panteghini and Bardella, 2015](#)).

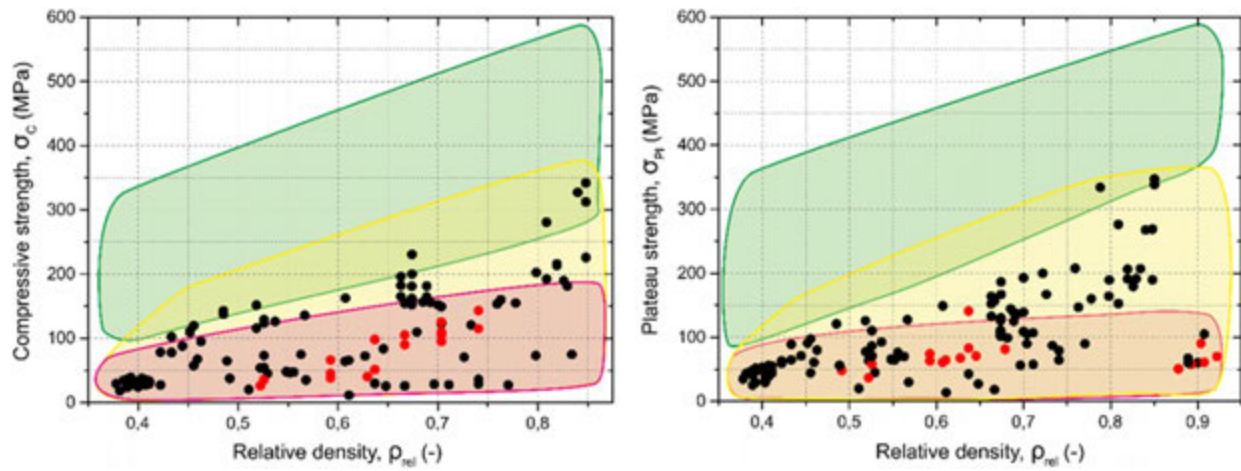


Fig. 7 Compressive (a) and plateau (b) strength of the MMCSFs in the function of the relative density.

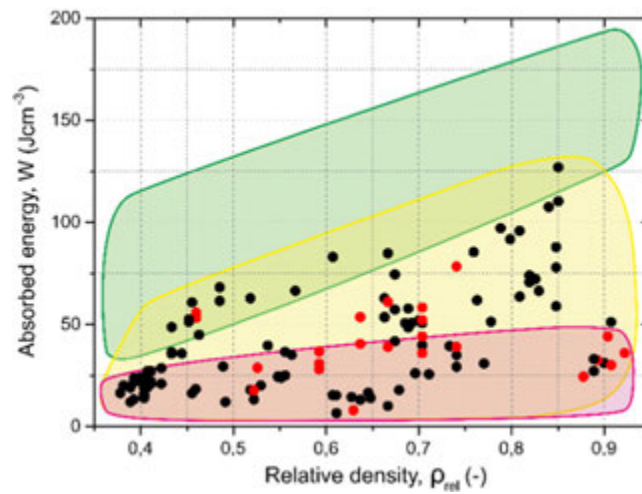


Fig. 8 Absorbed energy values of the MMCSFs in the function of the relative density.

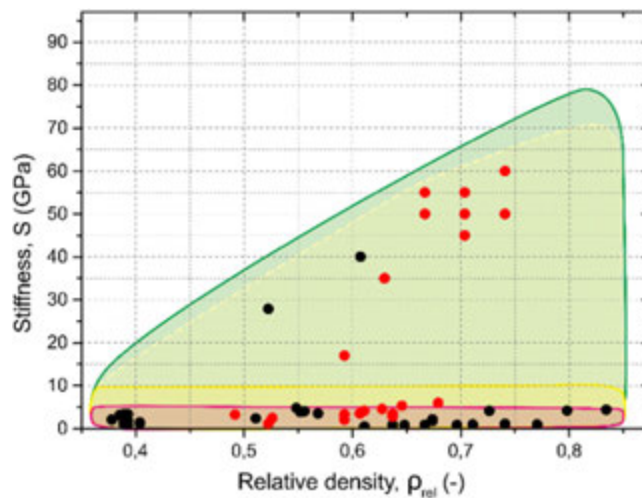


Fig. 9 Structural stiffness values of the MMCSFs in the function of the relative density.

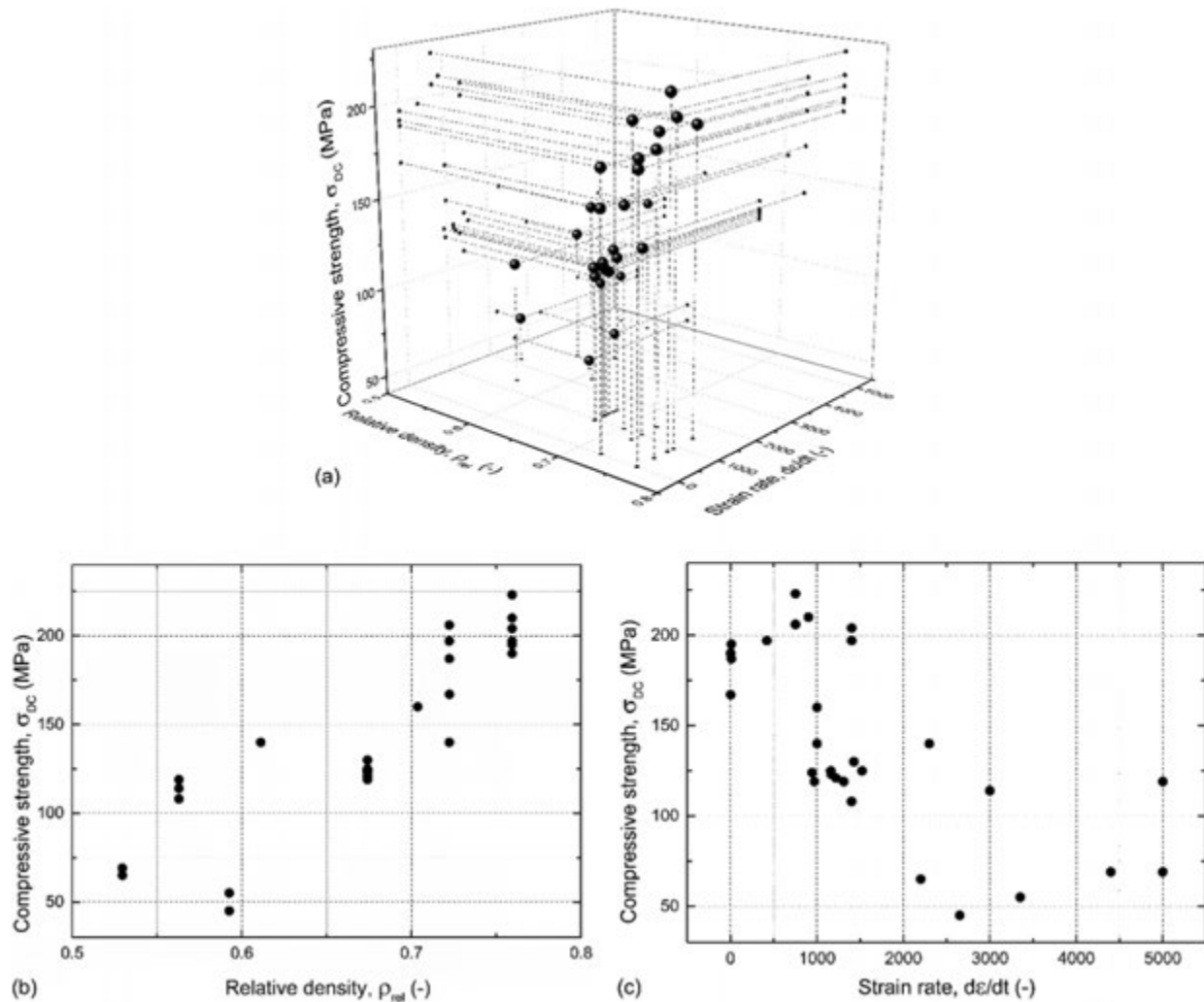


Fig. 10 Dynamic compressive strength values of the MMCSFs in the function of (a) the relative density and the strain rate, (b) the relative density and (c) the strain rate.

Besides the quasi-static properties of the MMCSFs, their behavior at high strain rates is extremely important. The strength and energy absorption values are determining in the case of MMCSFs used as collision dampers or as filler or absorber layers in defensive applications. The strain-rate sensitivity and the dynamic properties of MMCSFs are usually investigated by split-Hopkinson pressure bars. The dynamic strength values of the MMCSFs gathered from the literature (Dou *et al.*, 2007; Luong *et al.*, 2011; Goel *et al.*, 2012, 2014; Rabiei and Garcia-Avila, 2013; Zou *et al.*, 2013; Alvandi-Tabrizi and Rabiei, 2014; Cox *et al.*, 2014; Santa Maria *et al.*, 2014) and with respect to their relative density and strain rate are plotted in Fig. 10 (for better clarity, the values are also plotted separately in the function of relative and in the function of strain rate).

In general, and as it can be seen in Fig. 10, the dynamic compressive strength is increasing with the increasing relative density and – at least in trends – it is decreasing by the increasing strain rate. The dynamic absorbed energy (Fig. 11) values follow the same trends, the absorbed mechanical energy is increasing with the relative density and decreasing by the increasing strain rate.

It has to be mentioned to be correct: The dynamic absorbed energies are strongly depending on the deformation up to the end of the measurement (varies between ~20%–35% depending on the capacity of the testing apparatus).

The behavior of MMCSFs in the case of repetitive loading is at least as important as the previously mentioned mechanical properties. These properties are rarely investigated in the literature. For example, the effect of the matrix material and the size of the hollow filler spheres have been investigated (Katona *et al.*, 2017) in details and according to the ruling ASTM standards for the case of compressive cyclic loading. As results, the median curves and the fatigue strength have been registered. The technical purity Al99.5 matrix resulted in higher fatigue strengths than the more rigid, near eutectic AlSi12 matrix. Regarding the size of the reinforcing ceramic hollow spheres, the larger hollow spheres performed better (longer expected lifetime at the stress level above fatigue limit), because the smaller spheres are more vulnerable and the cracks have to propagate shorter distances within the ductile matrix to the next rigid ceramic hollow sphere. On the other hand, the cheaper, expanded perlite containing MMCSFs were also investigated (Taherishargh *et al.*, 2017b; Szlancsik *et al.*, 2018). Besides constructing the stress – number of cycles up to the

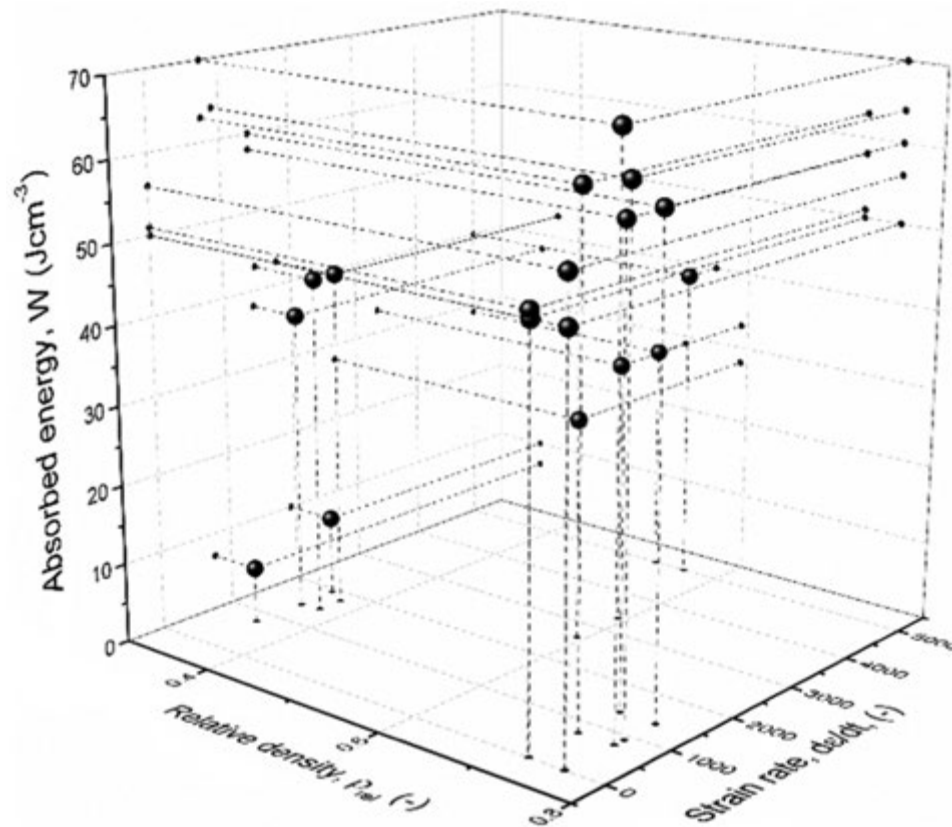


Fig. 11 Dynamic absorbed energy values of the MMCSFs in the function of the relative density and the strain rate.

failure curves at 50% probability level – the authors found that the registered curves can be classified into two significantly different types. The first type occurred at lower load levels and was shearing along a plane oriented at an angle of $\sim 45^\circ$ with respect to the loading direction. The second type was typical for high load occurred by the subsequent formation of two perpendicular shear bands. Besides these works Al and steel-based MMCSFs, filled by steel hollow spheres were produced (via casting and powder metallurgy) and tested (Vendra *et al.*, 2009). The main finding of the research was that under the repeated loading, the MMCSFs deformed by uniform plastic deformation and not along shear bands.

Since the machine parts are not homogenous geometrically and contain stress concentrators, the notch sensitivity of the MMCSFs have to be considered, but – according to the best knowledge of the author – only one article has been published on this problem (Szlancsik *et al.*, 2019). In this work, the effect of the notch geometry (“sharp,” V-shaped and “blunt,” U-shaped notches) and the effect of matrix material (Al99.5 and near eutectic AlSi12) were considered. The author has to note that, more papers are available connected to “conventional” metallic foams. In the referred paper, the authors utilize the fracture energy (the absorbed energy up to the compressive strength) and the elastic-plastic fracture toughness of the MMCSFs to describe the notch sensitivity. The main conclusion was that both of these properties are required to correctly describe the notch sensitivity of the MMCSFs. The fracture energy values (calculated by the numerical integration of the compressive engineering stress–engineering strain curves up to the compressive strength) were sensitive to the notch geometry, while the elastic–plastic fracture toughness was affected only by the matrix material. Interestingly, the U-shaped (blunter notches) resulted in lower elastic-plastic fracture toughness, because the larger surface of the U notch ensured the higher possibility to have a critical defect in the stress concentrator’s vicinity to initialize the crack.

Besides the structural applications, another initial aim behind the early development of MMCSFs was their application as some kind of “self-lubricating” material utilizing the opened hollow spheres on the surface as lubricant reservoirs to maintain wet lubricated condition for a longer time. In these publications, the effect of the amount and size of the hollow particles (fly-ash in the beginning) were investigated (Ramachandra and Radhakrishna, 2005, 2007). In the early investigations, the amount of the hollow particles was the main parameter besides the load, the run distance, velocity, and lubrication conditions (Rohatgi and Guo, 1997; Mondal *et al.*, 2009; Jha *et al.*, 2011). The mixed-oxide particles increased the surface and near-surface hardness of the samples even in small amounts. In most of the produced samples, the amount of fly-ash was below 15%. The performance of the samples has been compared to such classic metal matrix composites as Al matrix SiC filled composites (Jha *et al.*, 2011). The MMCSFs outperformed the metal matrix composites, especially in the dry condition when the coefficient of friction was proved to be one magnitude lower. The wear rates were proved to be lower in both lubricated and dry conditions as well.

Later, the investigations turned to utilize the hollow particles as lubricant reservoirs. In these publications (Májlinger, 2015; Májlinger *et al.*, 2016a,b), the more sophisticated hollow spheres (mixed-oxide and metallic) were mixed and studied in lubricated and dry conditions. The measurements revealed that despite the significantly ($\sim 65\%$ – 75%) smaller contact surface of the hybrid composites compared to pure AlSi12 samples, in lubricated conditions the MMCFs can be competitive materials for sliding parts. This is even more emphasized, when the high specific properties and there planned tailorability through the filling content and mixture are taken into account.

Summary

In summary, this article presented the production and properties of metal matrix composite syntactic foams (MMCSFs). As the MMCSFs are filled by hollow particles, they can be also considered as metal matrix composites. First, the constituents have been considered: The most commonly used matrices are Al alloys, besides Mg, Zn and Fe matrices are used and Ti and Cu matrices can be also found in the literature. Subsequently, the filler materials have been summarized, emphasizing their properties, advantages, and disadvantages. The matrices and fillers have been then joined to discuss the interface layers in MMCSFs. In the next section, the production methods of the MMCSFs have been grouped and discussed, emphasizing the potential of pressure die casting as a possible mass production method for MMCSFs. In the section about the structure of MMCSFs, the basic imaging methods and basic inner structures have been described and special structures such as hybrid MMCSFs and reinforced MMCSFs have been mentioned through the example of an advanced I-beam. Last, but not least, a general insight into the mechanical properties of MMCSFs has been given, discussing, in short, the quasi-static and dynamic properties of MMCSFs as well as their basic tribological behavior and features.

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Functionally Grade Composite Material Production

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Introduction to Functionally Grade Materials

Introduction

Materials play an important role in the life of human beings. In the past few years, there is a rapid development and applications of composite materials. Composites are solid materials that contain a reinforcement phase and a matrix phase. The reinforcing phase is in the forms of fibers, particles or sheets and is embedded in a matrix. The functionally graded materials (FGM) is a heterogeneous revolutionary material that belongs to the class of advanced engineering materials (Gayen *et al.*, 2019). FGMs exist in the nature and in the human body as teeth, bones, wood and bamboo. The enamel, outer surface of the teeth requires high resistance to wear and nature in a way has designed it as a functionally graded material to meet the expected requirements. The inside surface of the teeth is made ductile so that it acts as a shock absorber. The failure is initiated in the sharp interfaces of the composite materials. These sharp interfaces are sites where two materials are joined together and failure occurs. FGMs possess excellent characteristic to eliminate these defects by replacing these interfaces with a gradient surface which results in the smooth transition in the materials and with one material to another material. FGMs were first developed for the application in the thermal barriers. Nowadays, FGM is used in mineral processing industries where high wear resistance is required and in defense applications (Loh *et al.*, 2018). There are number of FGMs developed in the recent years i.e., functionally graded material, the microstructural gradient in functionally graded material, and the porosity gradient in functionally graded material (Deborah, 2003). There are different fabrication processes of FGMs depending on their areas of applications. With the improvement of these fabrication processes, the application of FGMs and its importance has increased as the overall cost during fabrication is reduced (Naebe and Shirvanimoghaddam, 2016).

History of Functionally Grade Materials

The concept of FGM was proposed as early as the 1980s in Japan for the space plane project for the usage in the thermal barrier. In that project, the composite required was to withstand a surface temperature of around 2000K and the temperature gradient required was of 1000K. At the time of testing, the traditional laminate composite materials had improper adhesion in them and the presence of sharp interface between the materials. Researchers replaced the sharp interface with some gradually changing interface that eliminated the high stress concentration sites. This change led to the development of FGMs. Early research on the development of FGM was reported in 1995 by Koizumi and Niino. In the next few decades, the FGMs then came into applications in the aerospace, medical, electrical, defense, sports industries. Most of the tissues and organs of the human body is made of naturally occurring FGMs. Bones and teeth are naturally occurring FGM in the human body (Sola *et al.*, 2016).

Types and Areas of Application of Functionally Grade Materials

Types of Functionally Grade Materials

The growing interest of FGMs in different areas has resulted in the development of various FGMs. The developed FGMs have varied mechanical, electrical, chemical and magnetic properties depending on their applications (Nikbakht *et al.*, 2019). The various types of FGMs i.e., porosity and pore size gradient structured FGMs, chemical gradient structured FGMs, and micro structural gradient structured FGMs are discussed briefly in the following subsections.

Porosity and pore size gradient materials

In the porosity gradient materials, the pore and the micro structural sizes are varied according to the required properties of the FGMs. The porosity is changed with respect to the spatial position of the materials. Porosity FGMs are prepared from the deposition of the powder with different pore sizes and pore shapes. This type of FGM is mostly used in the biomedical applications where the part or bone that is to be replaced includes porosity FGM so that there is integration and healing of the implant and the tissues (Mahamood and Akinlabi, 2017).

Chemical gradient materials

The chemical composition is varied in this type of FGMs in single or in multi phase materials. A single phase FGM is created when the composite is made from single phase due to the solubility of elements in one phase to another during sintering. The multiphase FGMs are widely used materials. The phases and compositions are varied within the material resulting in different phases with different compositions.

Micro structural gradient materials

In the microstructural gradient FGMs, the required properties are achieved by varying the microstructures gradually. The surface of the material is quenched for the microstructural gradation to take place. It can also be done through a controlled heat treatment process. The FGM microstructures are formed by allowing a liquid whose melting temperature is lower than the melting temperature of the titanium alloy. These types of FGMs find its applications in the case-hardened steel, cams or ring gear, bearings, and turbines where wear resistant hard surfaces and a tough core to resist the large impacts during the operation is required (Mahamood and Akinlabi, 2017).

Applications of Functionally Grade Materials

FGMs are the recent developments in the areas of the current and future applications. FGMs are regarded as the efficient and cost effective materials in the industrial sustainable development. The production costs of the FGMs are considered in the cutting tools, machining parts and engine components applications (Ebrahimi, 2016). The applications include in the field of biomedical, aerospace, defense, automobile, optoelectronics, marine industries. The porosity gradient FGMs are most frequently used in the biomedical applications. Living tissues like teeth and bones are widely replaceable from the damage of these parts or natural ageing. Biocompatible materials are needed to serve the purpose of the original tissues. Since the body parts that the materials replace are functionally graded materials, the majority of these materials are FGMs (Prasad *et al.*, 2018). FGMs can withstand very high thermal gradient making it suitable for aerospace applications. FGMs were first developed for the aerospace industry. Its usage has now increased in the rocket engine components, heat exchangers, turbine wheels, turbine blades, space shuttle, etc. (Ghatage *et al.*, 2020). FGMs have a characteristic property to prevent crack inhibition. This property of FGMs finds its application in the defense industry in bullet proof jackets, armor plates etc. (Mahamood and Akinlabi, 2017). The present usage of FGMs in the automobile industry is in the leaf springs, spark plugs, combustion chambers, flywheels etc. The body coatings of the vehicles also use FGMs. FGMs finds its applications in the components that are made from the optical fiber materials, photo detectors, semiconductors etc. In the marine industry, FGMs are used in the propeller shafts, the diving cylinders etc.

Production Methods of Functionally Grade Materials

Physical Vapor Deposition

FGMs have different fabrication processes for the two broad categories namely thin FGMs and bulk FGMs. The thin or thin surface coating FGMs are produced using different surface deposition processes i.e., physical vapor deposition, chemical vapor deposition methods etc. The bulk FGMs are produced by powder metallurgy, centrifugal casting methods, tape casting methods, solid freeform technology etc. In the physical vapor deposition technique, an atomized material is vaporized and deposited on the material for the production of the thin film coatings and thin FGMs. For the formation of FGM coatings, the solid material is vaporized from the surface until it disappears to be used as coatings. The atomization of the solid material deposited on the coating surfaces depends on the type of PVD techniques.

Chemical Vapor Deposition

In the chemical vapor deposition process the material to be coated is placed inside a vacuum chamber and the coating material vaporizes by heating the material or by reducing the pressure. The precursor gases are filled inside the chamber. The reactions happen on the heated surfaces of the substrate depositing the thin film on it. The byproduct reactants are exhausted outside the chamber with precursor gases. The derivatives of the CVD processes include metal organic chemical vapor deposition (MOCVD) process, the organo metallic chemical vapor deposition (OMCVD) process, the organo metallic vapor-phase epitaxy (OMVPE) process, and the metal organic vapor-phase epitaxy (MOVPE) process. Since the impurities are removed better than the PVD process, different varieties of materials with high deposition rates and with higher purity is achieved. The whole surface, the insides and the outer side surfaces are covered easily in this process.

Fabrication Process of Bulk Functionally Grade Materials

The physical vapor deposition and chemical vapor deposition methods are slow and energy intensive and is not economical to produce in the bulk functionally graded materials. FGMs are used to be required in extreme nature of the working environments. Some of the fabrication methods for producing bulk functionally graded materials are discussed in the following subsections.

Powder metallurgy

It is a technique to produce FGMs using three steps: weighing and mixing of the powders, stacking and ramming of the premixed-powders, and sintering. The powders or the graded materials are used as building blocks with varying size and compositions. A stepwise variation in composition in the green part is produced and sintering or hot pressing of the parts is done to achieve the consolidation process. Sintering is the heating of the green part so that some of the constituent materials of the FGM to melt. The thermodynamic factors during the sintering can also be made to design various types of the FGM. This method is cheap, ease in operation and requires less production time.

Centrifugal method

The centrifugal casting method is similar to centrifugal method where the solid or molten reinforcing material is poured inside the mold of a die which is rotating to form the functionally graded material. A centrifugal force is generated due to the rotation of the die. The molten metal is drawn towards the mold and gets separated in the suspended solid powders and the two material of different densities melts and hence the formation of the functionally graded material. The densities of the different materials, size of the particles and its distribution, solidification time and the molten materials viscosity influence the graded distribution of the FGM. Centrifugal casting method is classified into two another methods namely the centrifugal solid-particle method (CSPM) and the centrifugal in situ method (CISM). In the CSPM, the reinforcement powder particles remain solid in the liquid matrix so that reinforcement at the surface of the component and a core of the matrix material is produced. This results in the high wear-resistant material in the outer surface and high toughness at the core of the bulk material. The melting point of the reinforcement material is higher than the processing temperature of the material. In the CISM, the centrifugal force is applied during the solidification process. The density difference between the matrix and the reinforcing particles partially separates the materials in the liquid state. The gradient composition is formed before the crystallization of the primary crystals (Kirmizi *et al.*, 2019). These crystals in the matrix are formed due to the local chemical composition, and it is precipitated because of the density difference. The melting point of the reinforcement material is lower than the processing temperature of the material. The centrifugal casting method is effective in the production of the bulk functionally graded materials. The main disadvantage of this method is that only cylindrical sections are produced and there is limit to the formation of the gradient by the centrifugal force and the difference in the densities of the materials (Prabhu, 2017).

Tape casting method

In the tape casting method, the slurry mixture is prepared with the required powder mixture put into an organic solvent with binders and plasticizers and the slurry is spread onto a moving belt. A green part is formed after the solvent is dried. The belt passes under the edge of the casting blade and a tape of constant thickness is produced. The thickness ranges between 1 m to few mm. The stack of tapes with different mixture compositions forms the stepped gradients of FGM. To remove the organic binder and increase the density of the component, these tapes are then sintered in the high temperatures between 50° to 200°C and a pressure ranging between about 3–30 MPa. The tape casting method produces high resolution FGM but there is limitation to the strength of the component.

Solid freeform fabrication method

Due to some of the problems faced in the previous methods, research has been done to use alternative additive manufacturing methods known as solid freeform (SFF) method. Solid freeform is an additive manufacturing technique that involves five basic steps i.e., generation of the CAD model from design software, conversion of these CAD data to standard triangulation language (STL) file, slicing the file into 2D profiles, layer building of the part, and removal and finishing of the part. The laser based SFF process is generally used to fabricate FGMs. Laser cladding and selective laser melting produces components with high density. The SFF method has high utilization of materials to produce complicated parts with higher speed of production but there is poor surface finish of the components. This results in the secondary finishing operation at the end.

Advanced Manufacturing of Functionally Grade Materials**Additive Manufacturing**

Additive manufacturing (AM) of FGM can be defined as three dimensional industrial processes for printing and modeling using a computer controlled process or software like CAD and 3D object scanners. The 3D model data from the software program allows creation of such 3D objects by depositing materials in layers above each layer. It is also known by various names such as 3D printing, solid free form layered manufacturing, fabrication rapid prototyping and rapid manufacturing. This layer on layer manufacturing in AM eliminates the use of jig and fixture in the fabrication of complex parts in 3D geometry. A wide range of materials may be used in AM ranging from metals, ceramic, plastics to composites (Watnabe and Sato, 2009). Additive manufacturing comprises of four major methods for the production of FGM's namely:

(1) Material extrusion

Material extrusion is one of the most well-known additive manufacturing processes. Material extrusion usually uses a fused-deposition modeling for its AM processes. In these process spooled polymers are extruded, or drawn through a heated nozzle mounted on a movable arm. The nozzle moves horizontally while the bed moves vertically, allowing the melted material to be built layer after layer. Proper adhesion between layers occurs through precise temperature control or the use of chemical bonding agents. This AM technology is most commonly found in the domestic 3D. Material-extrusion processes of materials are cheaper. They are easily accessible and available. However the nozzle radius can sometimes limit the quality of the material. The accuracy of the final additive manufacturing of functionally graded materials part is limited by the material's nozzle thickness, the pressure of the extruded material affects the quality of the surface finish, and the process is slow in comparison to other processes (Watnabe and Sato, 2009).

(2) Powder-bed fusion

Powder Bed Fusion (PBF) technology is used in a variety of AM processes, including direct metal laser sintering (DMLS), selective laser sintering (SLS) etc. In powder bed fusion the powdered material is spread on a platform or a bed. Next a laser beam, or the electron beam, is used for scanning the path generated by the 2D CAD profile from the sliced 3D CAD file. The bed is lowered by a distance of the sheet thickness every time a layer scanned is completed. Fresh powders are then spread over the earlier scanned layer; and the scanning process is continued until the part-building development is finished. The fresh powder is supplied by the hopper or reservoir located below or beside the bed. A roller is used to spread the powder over the bed while the excess powder in the process is blasted away as the process continues.

(3) Directed energy deposition

The process of directed energy deposition (DED) is similar to material extrusion, although it can be used with a wider variety of materials, including polymers, ceramics and metals. It consists of energy source (laser, electron beam, or plasma arc) for melting the pool on the substrate. The powder or wire material, delivered into the melt pool is positioned coaxially with the energy source. The electron beam gun or laser mounted in this specific position helps in melting the wire or filament feedstock or powder. This helps in tracking of solid material upon solidification of the melt pool (Zhou *et al.*, 2018). DED also include the laser-metal deposition process (LMD), also known as direct-metal deposition, or directed-light fabrication. It is responsible for net shaping technology and electron-beam deposition. DED can be used to mend high valued mechanisms which were not repairable earlier. They are also used for product remanufacturing i.e. it is capable of building a new material on an existing material base.

(4) Sheet lamination

Sheet lamination is yet another class of additive manufacturing. It comprises of two main different methods namely laminated object manufacturing (LOM) and ultrasonic additive manufacturing (UAM). In LOM an alternating layers of paper and adhesive is used, while for UAM ultrasonic welding is used for conjoining thin metal sheets. In the LOM process, a heated roller is used to bond and stick the adhesive-coated sheets together. The required structure is then cut with the help of a laser according to the path generated in the CAD digital data. The LOM process is a self supporting system. The excess sheet material from the cut sheet material helps to form the needed support structure for the overhangs and the undercuts. Such system provides an effective, cheap and fast process of AM. While the LOM process uses a roller blade to stick the sheets. The ultrasonic additive manufacturing (UAM) process utilize ultrasonic welding process to join or stick the sheets or ribbons of metal, such as Al, stainless steel, Cu and even titanium etc. The UAM processes require further CNC machining process and milling process for the removal and well rounding of the idle materials during the process. Unlike the LOM, the UAM process is a low-temperature process. Further advantage of such process is that the UAM is a relatively low energy process as it uses a combination of ultrasonic frequency and pressure and does not involve melting the materials (Watnabe and Sato, 2009).

Laser Metal Deposition Process

Laser metal deposition (LMD) belongs to the directed energy deposition category of the additional manufacturing. The main characteristic of such process is the use of laser as it name suggests (Ramakrishnan and Dinda, 2019). The metal powder injected in the metal surface or metallic substrate is melted by the laser beam. The absorbed metal powder produces a deposit on the surface. It then produces the required 3D structure from the 3D CAD modeling by adding the materials in layers like the above processes. LMD provides as an excellent alternative for the processing of titanium and its alloy and is replacing various conventional manufacturing processes such as gas metal arc welding and thermal spraying (Yan *et al.*, 2020). LMD is also capable of handling more than one material at a time. It can produce complex part at the same time while manufacturing the FGM in a single step (Li *et al.*, 2019). The LMD is a continuous FGM production process.

Friction Stir Processing

Friction stir processing (FSP) is a newly developed technique in the fabrication of FGM's. FSP is a localized micro structural modification that leads in the steady property modification of the overall material. FSP is based on the friction stir welding process that allows local modification of microstructures in the near surface layers as well as control the modification period. Extreme stirring is involved to disperse reinforcement into the metal matrix. However, very extreme stirring might lead to irregular results and disruption in the presence of unlike reinforcement like in visco-plastic material. A well known term associated with FSP is "overlapping". FSP undergoes different passes which results in overlapping of metal, composites, matrix etc. The tool used in FSP consist of two side: retreating side (RS) and advancing side (AS). Overlapping on different sides produces different surface topography or profile. In the AS, recrystallized zone is extended and it is visually smoother profile with sharp appearance. While the RS presents us an irregular wave profile. Therefore we can say that overlapping can determine the mechanical properties as well as the surface finish. FSP is use to develop the mechanical property of the matrix compared to its base material. It provides as an effectual treatment in achieving chief micro structural refinement, density and homogeneity at the processed zone. It also allows the eradication of defects in the manufacturing process. Further advantages provided by the FSP are improved hardness, improved tensile strength, better fatigue, wear and corrosion resistant and an environmental friendly process (Sharma *et al.*, 2017).

Centrifugal Mixed Powder Method

Centrifugal mixed powder method works on the principle of centrifugal casting technique. It is used for the fabrication of FGM especially containing nano particles is difficult to fabricate. A spinning mould is an apparatus where the whole processes take place where the powder mixture of functional nano-particles and metal matrix particles is inserted. A metal matrix ingot is then melted and poured into the spinning mould containing the powder mixture. The molten metal matrix penetrates into the space between the particles. As it penetrates the molten matrix melts the metal matrix powder. As a result we obtain a FGM matrix with nano particles distributed on its surface. Centrifugal mixed powder technique can also be applied for the fabrication and processing of, Cu/SiC and Al/TiO₂ etc.

Centrifugal Sintered Casting Method

Centrifugal sintered casting method is a modified version of centrifugal mixed powder method. The processing and fabrication of FGM are achieved by the combination of two processes, i.e., centrifugal sintering and centrifugal casting. The powder mixture in the previous discussed process is likely to flow away during the centrifugal casting process. Hence centrifugal sintering was introduced to curb this effect (Ram *et al.*, 2019). A molten material containing a different reinforcing material is poured inside the rotating die either in molten or in solid state. A centrifugal force is produced as an effect of the rotating die. This force along with the different densities in the materials helps in drawing the molten material towards the mold as well as creates division in the suspended solid powder material. The graded distribution of the functionally graded material formed by the centrifugal casting method would be significantly influenced by.

- (1) The processing parameters.
- (2) Difference in density between the reinforcing powder particles and the molten material.
- (3) The particle size and the particle size distribution of the powder.
- (4) The viscosity of the molten material.
- (5) The solidification time.
- (6) The matrix and that of the reinforcing material.
- (7) The speed of rotation of the die.

The centrifugal casting method is one of the most efficient methods for processing bulk of the functionally graded materials due to its extensive range control of composition and microstructure. There are two types of fabrication of a FGM when using the centrifugal casting method, namely the centrifugal solid-particle method (CSPM) and the centrifugal in situ method (CISM). In the CSPM method, the melting point of the reinforcement material is significantly higher than the processing temperature, and the reinforcing powder particles remain solid in the liquid matrix. This helps to fabricate selective reinforcement at the surface of the component, with a core more than matrix material. The selective reinforcement of the component surface helps to fabricate a high wear-resistant material in the outer surface, while maintaining high toughness at the core of the bulk material (Sasidharan *et al.*, 2018). A steeper compositional gradient is produced with the CSPM method because the motion of the solid particles during the rotation under the centrifugal force is governed by Stokes's law. This means that the larger the particle size, the larger the migration distance. The processing parameters controlling such process are the particle size and the distribution of the reinforcing material (Ichiro and Yoshinari, 1996).

Future Research Directions in Functionally Grade Materials

The FGM are usually made as composites hence they provide as an excellent improved alternative to material previously used. It was developed to solve the limitations that were posed by the conventional composite materials. Furthermore there exist unlimited future scope of modification and fabrication of such composites known and unknown. FGM offers as a thin coating application or as a volume material, depending on the intended application area. FGMs could also be developed through the gradation in porosity in the material. Material properties, such as the elastic modulus, the thermal expansion behavior, the reduced density and the improved hardness can be achieved with FGM. This helps in producing a material with superior and multiple properties without any structure of weak interface (Li *et al.*, 2020). The actual concept of FGM was acquired from nature and used to solve engineering problems in the same way that nature has used such materials based on their application requirement and areas of application. The application of FGM in thin film coatings has helped to reduce stress, prevent the peeling of the coated layer with time; and it also helps to prevent micro crack formation and the proliferation of cracks. The FGM can also be produced through the use of an advanced manufacturing process known as the additive manufacturing process. The main advantage of the additive manufacturing process is that it can be used to produce FGM no matter the complexity in a single manufacturing run. The cost of FGM is still very high due to the high cost of the powder processing and on the fabrication methods. However in the production of FGM is the additive manufacturing process reducing some of this financial saddle and future useful researches. The application of FGM could be extended to some of the capable materials of structures and infrastructures for the practical purpose of sound resistance, heat insulation and fireproofing applications (Ebrahimi, 2016).

Conclusion

Functional graded materials were not produced overnight. They are the results of a long list of failed experiments. However, despite that the urge to produce a better modified version of composite materials and matrixes has never stopped researchers nor scientist

to give up the topic. FGM has a whole lot of structural and physical properties that attracts the researchers for the present and current work and will ever be the topic of interest for engineers and researches. We now can build a structure that is lighter in weight yet harder than its base material. This provide as an excellent alternate to heavier material. The application and uses of FGMs are immense, from aerospace industries, engineering structures, automobile industries to paint and oil industries. The advances in technology have added impetus to the development and usage of FGMs. 3D printers, and 3D modeling can now be used for the fabrication of this FGMs. New coating techniques and surface modifications have added extra value to the marketing and processing of matrixes and composites. FGM therefore have a strong future in structural engineering applications and naturally the curiosity and eagerness of human will not be limited to what we have already achieved.

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Development of Polymer Composites by Additive Manufacturing Process

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Nomenclature

ABS Acrylonitrile butadiene styrene
AM Additive manufacturing
BAAM Big area additive manufacturing
CAD Computer aided design
FDM Fused deposition modeling
LOM Laminated object manufacturing

PC Poly carbonate
PEEK Polyether Ether Keytone
PLA Polylactic acid
PVB Polyvinyl butyral
SLA Sterolithography
SLS Selective laser sintering
STL Standard tessellation language

Introduction

The advancement of conventional manufacturing industry has seen vast development with increased manufacturing parts within the stipulated time and reduction in manufacturing cost, there still remain set of complications that cannot be addressed by using conventional manufacturing techniques. Production of limited number of parts with reduced cost, development of one-of-a-kind specimen and manufacturing of parts at place of requirement are some of the hindrances that conventional manufacturing system finds difficult to address. Development and analysis of heat exchanger with optimization can be done by using software packages that include computational fluid dynamics, to develop this model in one piece using casting, forging or machining is tedious task. Joining of two or more parts could lead to one of the following deformities; design complexity, stress concentration in joints and/or leakage of fluids. This is one among many examples that has led to compromises in development of new designs using conventional methods (Spowart *et al.*, 2018).

Additive manufacturing or more commonly called as 3D printing is comparatively a new, advanced, sustainable, and green technology in the prospects of manufacturing sector. The core idea of this method of building up a material is basically to reduce down the material wastage and construct the required material of any complex geometry in a layer by layer format (Standard, 2012; Hull, 1986). The ISO/ASTM52900-15 has classified the process of AM into 7 categories which uses various process of manufacturing a material; however, there exists few commonalities: development of CAD model, conversion to STL (standard tessellation language), and feeding the model to printer (ISO/ASTM, 2015), the above steps give a great edge in controlling the requirement of material and also flexible process parameters. Fig. 1 shows the classification of AM, the selection of material for AM depends on the material requirement, process parameters, speed of development, performance and cost, dimensional accuracy, utilization of final product and its applications (Sood *et al.*, 2010).

Major companies across the world have tried their hand in 3D printing such as 3D printed line lamp by Philips, customized instrument and spacecraft parts built by NASA, Nike 3D printed a part for its shoe. 3D printing has made inbound roads into larger field of

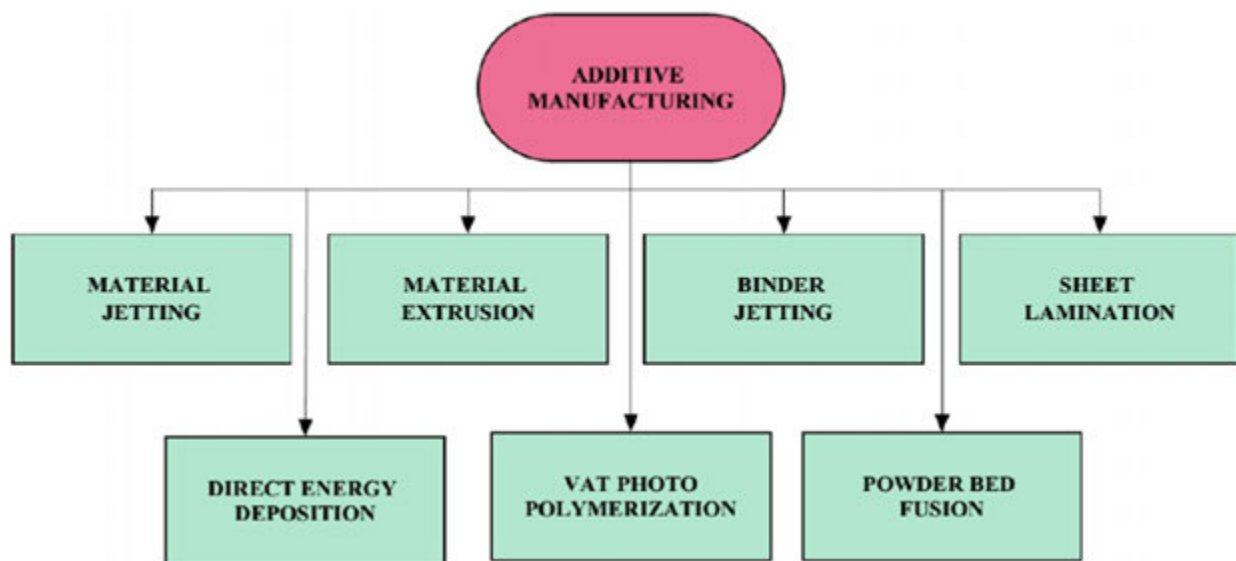


Fig. 1 Classification of AM.

manufacturing with minimal wastages; however, the polymer based manufacturing using FDM (Fused Deposition Modeling) has made a larger impact on the globe when compared to other forms of AM, there are rising number of global and local manufacturers of 3D printers who can build and give the parts, develop innovative materials and also sell the 3D printers of their own. Every miniscule sector is able to use this technology for the betterment of either existing component or in totality to build a new one (de Jong and de Bruijn, 2013).

AM manufacturing uses a wide variety of materials for development of products such as polymer, ceramic, metals, etc. The choice of material further depends on the required strength, properties of material, build rates, and above all the area of application (Piller *et al.*, 2015). Polymers are most commonly used materials in additive manufacturing industry, due to its ease of diverse adoption to various processes of manufacturing. The raw feed of polymers to numerous category of utilization can be seen in the form of filaments, powders, resins, and reactive agents. Fused deposition modeling (FDM), Stereo lithography (SLA), 3D inkjet technology, and Selective laser sintering (SLS) are the methods for development of polymer and its composites using the concept of additive manufacturing (Lee *et al.*, 2017a).

On the other perspective looking at the utilization and advantages of additive manufacturing over conventional manufacturing Mohsen Attaran has elaborately discussed about the advent of additive manufacturing technologies and its uptrend in shifting the conventional manufacturing system to additive manufacturing in global scale. The disruptive change is going to occur in the field of supply chain, lead time, designs, and customer based demand. Advantages of AM over conventional manufacturing system are summarized in Table 1 (Attaran, 2017; King, 2012).

Processing

AM uses a choice of materials for the production of either functional parts or prototypes; through numerous methods of development which is shown in Table 2. The advantage of AM surpasses the conventional method in many forms, development of any complex geometry without the requirement of assembly, reduced wastage plays an important role in enhancing the sustainability and green technology of manufacturing by reduced utilization of chemicals for clean-up and engraving and hence reducing the carbon footprint (Babu *et al.*, 2015). Polymers are the most commonly used resources for AM. The following sections discuss the process that use polymer as a raw material for development of parts.

Table 1 Advantages of AM over conventional manufacturing

Parameter	Advantages over conventional manufacturing
Micro manufacturer	Consumers have the ability to become micro manufacturers by developing a small worn part of the purchased product.
On requirement/demand manufacturing	Cost reduction in terms of stocking and transport of replacement parts is drastically reduced as AM facilitates the capability to develop parts on requirement or demand.
Precise and required component for manufacturing sector	Very low tolerance and complex parts can be easily developed according to requirement. Aerospace and automotive manufacturing sector have 20% of components through AM.
Paradigm shift from consumer to producer – consumer	After market services have been slowly shifting from central oriented to consumer producing oriented.
Design and redesign	Reduced time and cost penalties for innovative design approval over any stage of manufacturing. Unlike conventional manufacturing which involves huge cost and time delay.
Sustainability	Smaller ill effect on the environment as the utilization of part is only what is needed unlike conventional in which full part has to be manufactured.
Complex geometry	Any kind of complex geometry could be developed without any machine or model interference.

Table 2 Polymer Materials and Applications of Additive Manufacturing

Process	Materials	Applications
Vat Polymerization (Stereolithography)	Photo Curable Polymers, acrylated epoxy.	Medical models, photoresists, digital imaging.
Powder Bed Fusion (Selective Laser Sintering, Selective Laser Melting, Electron Beam Melting)	Polyether Ether Keytone (PEEK), Nylon, PA6 and 12.	Turbine blades, wind tunnel models, manufacture of jigs and fixtures.
Sheet Lamination (Laminated Object Manufacturing, Ultrasonic Consolidation)	PVC, paper.	Micro Heat Exchangers, cell phone cases.
Material Extrusion (FDM)	Acrylonitrile Butadiene Styrene, Polylactic Acid, Poly carbonate, Nylon.	Prototypes and mechanical parts, plastic fins, cooling channels.

Note: Klimek, L., Klein, H.M., Schneider, W., *et al.*, 1993. Stereolithographic modelling for reconstructive head surgery. *Acta Otorhinolaryngology Belg* 47 (3), 329–334. Lim, S., Buswell, R.A., Le, T.T., *et al.*, 2012. Developments in construction-scale additive manufacturing processes. *Automation in Construction* 21 (1), 262–268. Van Noort, R., 2012. The future of dental devices is digital. *Dental Materials* 28 (1), 3–12. doi:10.1016/j.dental.2011.10.014. (Epub November 26, 2011. Review). Bai, Y., Wagner, G., Williams, C.B., 2015. Effect of bimodal powder mixture on powder packing density and sintered density in binder jetting of metals. In: *Proceedings of the Annual International Solid Freeform Fabrication Symposium*, vol. 62, pp. 758–771. Wong, K.V., Hernandez, A., 2012. A review of additive manufacturing. *ISRN Mechanical Engineering* 2012, 10, 208760.

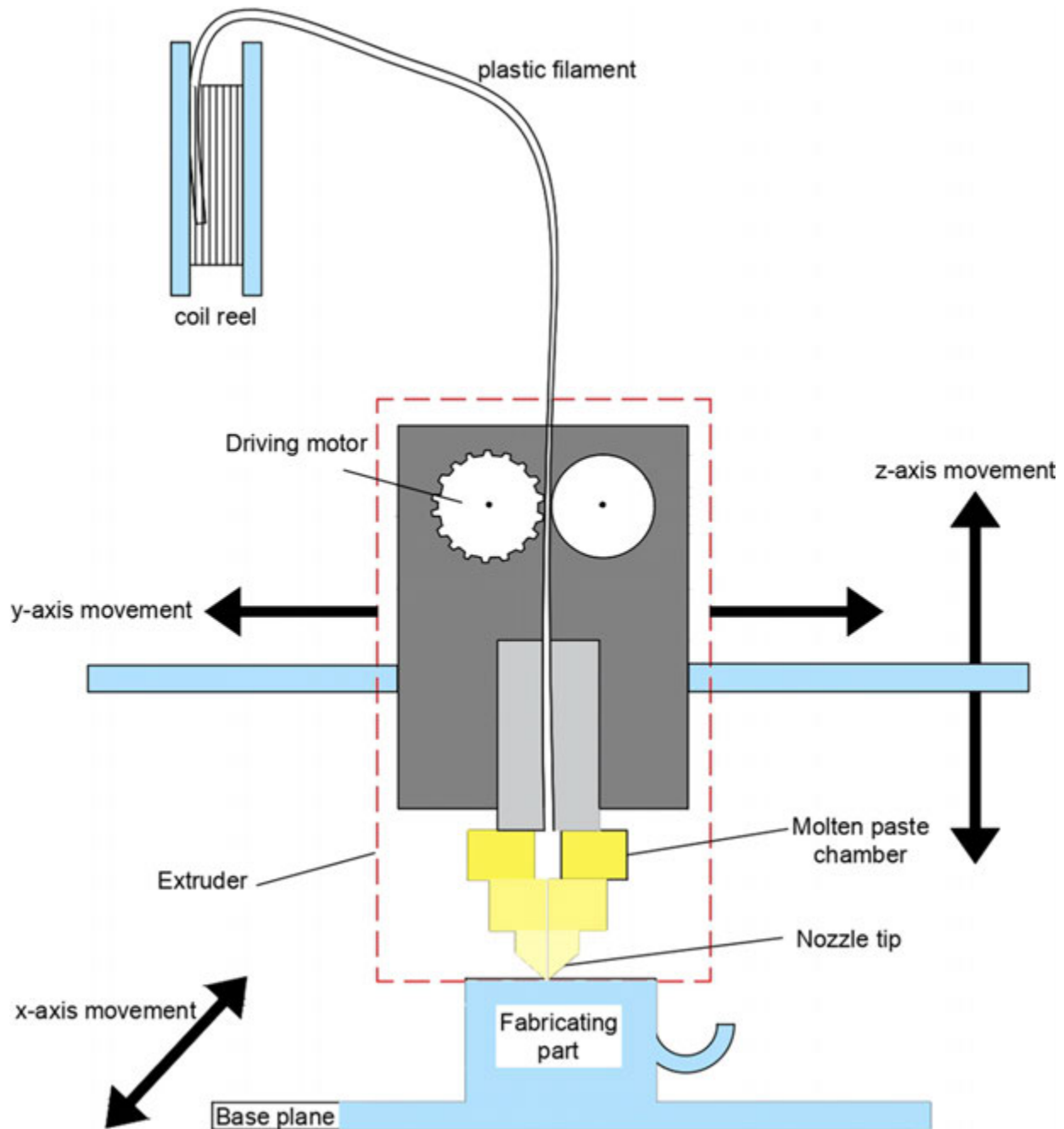


Fig. 2 Line diagram representing working principle of FDM.

Fused Deposition Modeling (FDM)

FDM the most commonly used printer's uses polymer for fabricating the materials in any form of design. The process of fabricating the parts by FDM is done layer by layer. The commonly used materials such as PLA (Polylactic Acid), ABS (Acrylonitrile Butadiene Styrene), Nylon, PC(Poly Carbonate), etc., are to be drawn in the form of filament of either 1.75 or 2.85 mm diameter depending on the specification of FDM used. The filament is passed through the nozzle which is heated to a certain temperature that melts to a semi liquid state and the material is let on the fabrication bed which is again maintained at various temperatures depending on the kind of polymer used. Once the first layer of the specified thickness is laid down along x and y axis the nozzle moves up by a layer thickness in z direction and makes the next layer of material to deposit on it. The layers get bonded together by cooling and then solidify until the final layer is laid down (Wang *et al.*, 2017). The properties of fabricated parts can be controlled by controlling process parameters like layer thickness, raster angle, orientation, air gap, and width of raster (Sood *et al.*, 2013). Fig. 2 indicates the line diagram of FDM.

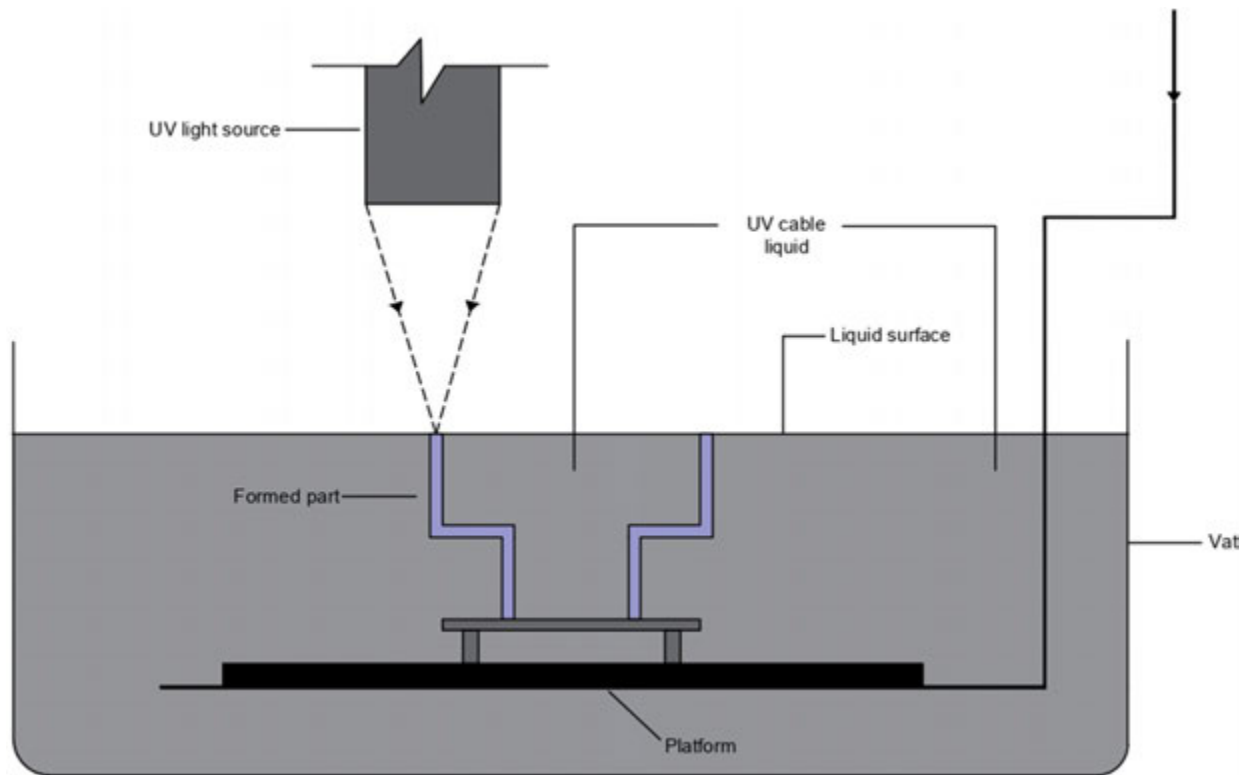


Fig. 3 Stereolithography working mechanism representation.

The added advantages of polymers over any other material include lightweight, robustness, flexibility, easy availability which has made its application in vast domains. It is used in aerospace industry, architectural areas and automotive industry and even in the field of medical sciences (Wong and Hernandez, 2012; Murphy and Atala, 2014).

Stereolithography

The method of Stereolithography came into development stage in the year 1986. Solution of resin or monomers is used as feed material, over which an electron beam or ultra violet light is focused. The required intensity of the beam instantly activates the monomer chain into polymer chain. The process of polymerization is followed by formation of solid layer which further holds the subsequent layers. Post processing is carried out to enhance the properties of the mechanical and physical behavior of the developed part. The thickness of each layer depends on the energy level of the exposed beam or light (Melchels *et al.*, 2010). The working line diagram of this process is indicated in Fig. 3.

Selective Laser Sintering

Powder bed fusion process consists of spreading out the powder on the platform which is bound together by the binder or a beam. Successive layers are rolled upon the first layer and are used until final part is formed. Post processing is carried out to remove the excess powder. To fine tune the part sintering, coating or infiltration is carried out. Laser is also used for the polymers with low melting points. Laser enhances the surface temperature of the powder and forms a bond at molecular level. The developed parts are denser in comparison to other process (Utela *et al.*, 2008; Lee *et al.*, 2017b). Fig. 4 shows the process of Selective Laser Sintering under the category of powder bed fusion.

Laminated Object Manufacturing

Polymers can also be used as raw material for manufacturing through laminated object manufacturing. The material to be used should be in the form of continuous sheet. Adhesive plays an important role in determining the strength of the developed part as each layer is coated with the adhesive that is laid according to the chosen thickness. The layer is cut on the defined thickness and then bonded together either with the help of laser or blade and then by applying the pressure. One of the foremost commercially available methods for development of parts using additive manufacturing is LOM. Post processing of the materials is required for formation of precise dimension (Gibson *et al.*, 2015). Overall, the method is best suited for

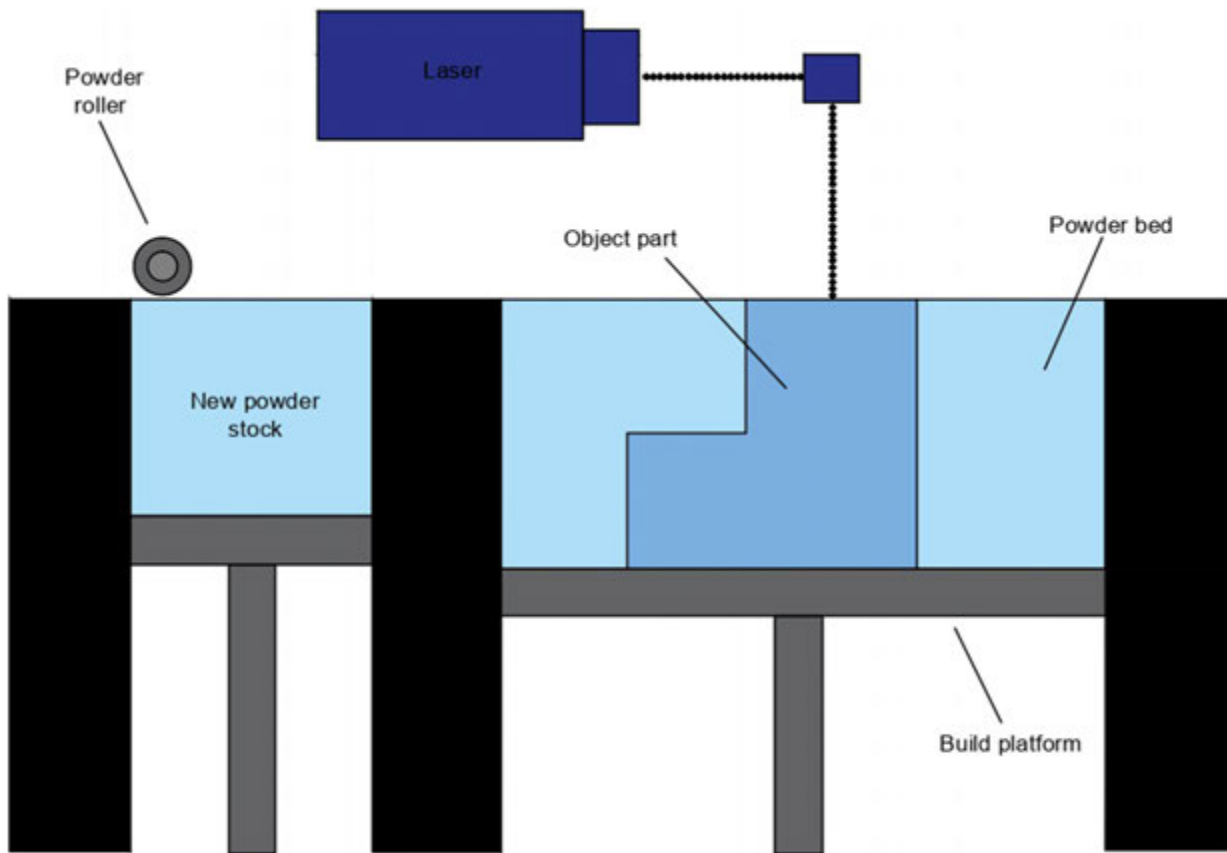


Fig. 4 Selective Laser Sintering process.

development of models of prototypes or non functional parts. Complex geometry and hollow structures are difficult to develop using this method. Fig. 5 gives a working principle of LOM process.

Need for Polymer Composites and its Advantages

The utilization of efficient materials through AM needs to gain a rapid momentum. The exponential advancements by researchers to use these parts for functional applications is increasing to the level of utilization of structural supports in architectural design mainstream and chassis manufacturing for automobiles. However, the main scale application of polymers in load bearing industries and as a functional part still remains a void. This drawback has led the utilization of 3D printed polymer parts only to the scope of prototype. Hence, exploitation of new materials is possible by using composite polymer materials that enhances the overall mechanical and thermal properties of the fabricated parts.

The area of exploration of AM has surpassed various obstacles and reached a level of manufacturing; to an extent of producing a car chassis of a vehicle; big area additive manufacturing (BAAM) has paved a way for this, which has developed a two seater electric car chassis. The possibilities of developing such a kind of product is possible only by developing a composite material which eventually enhances the required properties. The utilization of polymer has seen a wide area of application as discussed earlier; however, the main drawback of polymers is poor quality of heat dissipation and higher coefficients of thermal expansion. These hindrances play a major setback in direct utilization of polymer in thermal applications of electronic devices which utilize high power density and require rapid heat transfer; miniaturization of smart tools has led to overheating of devices which results in system failure or reduced lifetime (Schubert *et al.*, 2008; Chung, 2001). Considering these factors there is a need for enhancing the properties, which is possible by building a composite of specific materials. Numerous researchers have tried the combination of matrix and reinforcement to augment the desirable characteristics.

The addition of reinforcement to the matrix to improve the characters may be of varied forms such as micro particles, fibers, nano particles, etc., which may be either in the form of powder, spherical shape, whiskers or platelets. There comes a large variation of properties with addition of these reinforcements in the field of mechanical properties or thermal properties. A comparative study was done to notice the change in tensile strength of ABS polymer by the addition of short fibers in wt%. It was keenly observed that 10 wt% addition of nano fiber increased the tensile strength by 39% (Zhong *et al.*, 2001). Another comparative study was made between compression molding and FDM with respect to void formation, fiber length, and fiber distribution. 10, 20, 30 and 40 wt% of short carbon fiber were mixed with ABS polymer. There was an observation stating an increase in tensile property with every

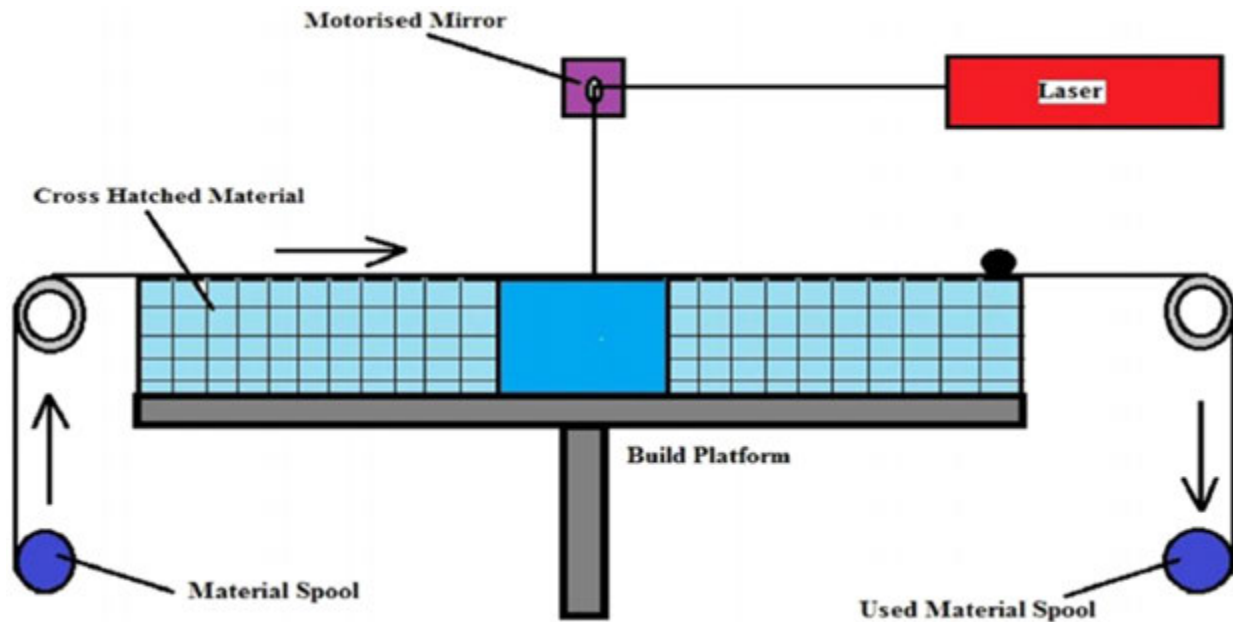


Fig. 5 Laminated Object Manufacturing process.

10 wt% addition of carbon fiber. However, there was a problem through FDM for 40 wt% of carbon fiber because of clogging of nozzle. FDM process showed higher fiber orientation property when compared to conventional manufacturing. The increase of tensile and modulus properties predicts the usage of this composite for load bearing parts (Tekinalp *et al.*, 2014).

FDM a simple to look at but indeed a complex process phenomenon has captured the global market for its easy utilization for different kind of polymer and their blends. The designer basically observes for efficient utilization of the machine which respect to its dimensional accuracy, surface finish, lesser wastage of materials, enhanced productivity rates with reduction in cost and time. The above mentioned parameters could be achieved by FDM; however, optimization of the process parameters is of much need for accurate fabricated parts. Mohamed *et al.* (2015) have made extensive literature survey on the parameters that bring out the effective results for fabricated part by FDM. They have concluded that process parameters such as lay up speed, raster angle, and width and air gap play a significant role in enhancing the outcome. However, the research has been carried out exhaustively for mechanical parameters, still there remains a huge void in determining the thermal, chemical, and dynamic parameters. The large utilization of polymer in the process of FDM has led to development of brittle and anisotropic parts. The reason for these properties has been understood to be influenced by the process parameters such as orientation, thickness, raster angle and width, and air gap. The formation of bond between the layers in FDM process plays an important role in determining the prosperities of the end product. Temperature variation between the layers has been observed which is beautifully explained as follows, the solidification of the layer takes place on the build bed as the first layer is led upon of a particular thickness, due to modes of heat transfer, then second layer is led upon it which is having a higher temperature than the solidified layer and it imparts its heat to the solidified layer which results in re-melting that causes the uneven surface finish between the layers and may lead to formation of air gap as well due to thermal distortions. The most selective values have been stated as follows; for layer thickness 0.254 mm, orientation 0.036° , raster angle 59.44° , raster width 0.422 mm and air gap 0.00026 mm (Sood *et al.*, 2012).

Keshavamurthy *et al.* (2015) have studied and experimented the optimization of process parameters; considering orientation angle, layer thickness, and fill angle as the variables. Taguchi method of design optimization was inculcated for analyzing the optimal characteristics for higher tensile strength, greater dimensional accuracy, lesser surface roughness, and least manufacturing time. The following percentage contribution were stated to be optimal for tensile strength; 37.33% orientation angle, 28.35% fill angle, and 34.3% layer thickness, for dimensional accuracy 75.52% layer thickness, 13.11% orientation, and 11.67% fill angle, for surface roughness 88.45% layer thickness, 7.55% orientation, and 4.09% fill angle, for manufacturing time 38.45% layer thickness, 26.83% orientation angle, and 5.47% fill angle. Li *et al.* (2017) made a very impactful study on behavior of thermal properties of Graphene polymer composites. Graphene being on elevated list for its thermal conductive property plays a significant role in enhancing the thermal properties of the GPC. Thermal conductivity of the polymer with graphene as reinforcement can increase the property if only the filler material is above the percolation threshold. Authors have clarified that the molecular interaction with transfer of heat can be attained if only the chain of reinforced molecule is arranged without any cross links from surface to surface. The understanding is further clarified by stating that the orientation of the layers also plays a very important role in expanding the thermal characters. The need for efficient thermal materials is of greater importance in electronic packaging industry, thermal energy storage, batteries, etc. Implementation of biocompatible parts has been on the study for many researchers. ABS (Acrylonitrile Butadiene Styrene) is most commonly used polymer in the process of FDM. Using ABS for medical implantations is still a void in medical industry, as to see the

effects of using ABS as an internal body part. The toxicity of using ABS is nil till date; however, few medical researchers claim styrene molecules in ABS reacts and seems to be carcinogenic. Hence, poly lactic acid (PLA) and polycaprolactone (PCL) was used for manufacture of biocompatible parts which showed lesser porosity and nil adverse effects to be used as an implant (D avila *et al.*, 2016; Huff and Infante, 2011; Drummer *et al.*, 2012). The main parameters of concern for using fused deposition modeling are the printing area, printing speed and the rate at which the material flows off the nozzle. Big area additive manufacturing (BAAM) in alliance with Cincinnati Incorporated has developed a large scale manufacture system which can build with a scale of 6 m length $\times$ 2.5 m width $\times$ 1.8 m height, with output flow of material at a rate of 45 kg/h (Cincinnati Incorporated, 2016). In the similar lines Thermwood developed a large scale model with flow rate up to 266 kg/h. the maximum build area of this machine is 30 m length $\times$ 3 m wide $\times$ 1.5 m height. The system is developed in such a way that CNC router and printer head are in the same gantry system of the model (Thermwood, 2016).

Few researchers have developed a filament of single walled carbon nanotube reinforced with ABS for FDM. 10 wt% of carbon nanotube filament was added as optimal percent and was reported for improved results in mechanical properties. They noted reduction in porosity and proper alignment of filler material in the filament which was the reason for rising of mechanical properties of the developed filament (Shofner *et al.*, 2003). There is a need for improvised polymers in the field of thermal application. Alumina, silicon carbide, and numerous carbon based material have been tried as reinforcement for polymers among which diamond displays higher conductivity and stability and hence is used as polymer reinforcement for thermal applications (Kalsoom *et al.*, 2016). Tambrallimath *et al.* (2018) have studied the variation of thermal conductivity of the polymer composite developed by FDM. Copper as reinforcement was added to the ABS matrix and with the help of parallel conductance method, thermal conductivity was noted. It was found that ABS + 5 wt% Cu exhibited better thermal conductivity than pure ABS. Carneiro *et al.* (2015) by utilization of design of experiments developed a composite by addition of carbon fiber reinforcement to epoxy matrix. The principle of study was to identify the factors affecting the preferential alignment of fibers in the epoxy during the extrusion. Translational speed, loading of the reinforcement, and the diameter of nozzle were the parameters that would determine the orientation of fiber. The researchers also suggest that increment in loading of reinforcement and enhancing the length of fiber could improvise the orientation of carbon fiber in epoxy matrix.

Numerous studies have been carried out by researchers to enhance the properties of polymers by addition of filler material. A comprehensive review verifies the ability of enhancement of mechanical properties in terms of tensile and flexural strength; however, the dependency of this improvement largely depends on porosity and build orientation (Yasa and Ersoy, 2018). Vijay *et al.* have made an experimental study by addition of graphene to PC-ABS. up to 0.25 vol% of graphene was successfully added to the matrix and the filament was extruded through the process of compounding and extrusion. The dispersion characters of the composite were studied. The density of the composite increased with increase in the filler content (Tambrallimath *et al.*, 2019). There still remains a wide scope of interest for finding the possible ways of preparation of filament for numerous applications of choice.

Sterolithography method used for manufacture of polymer parts has lower mechanical properties in comparison to the parts developed by conventional methods. The property enhancement was observed with addition of various filler materials in a randomized order to improve the properties. Eng *et al.* have used plate shaped montmorillonite nanoclays with photopolymer which were mixed with numerous methods and were dispersed homogeneously. The load bearing capacity of the plate shaped structure is evenly utilized. The specimens tested exhibited an increment in elongation by more than 100% and also the improvements were seen in tensile and Young's modulus properties along X-Y plane of the specimen. This kind of research paves the way for utilizing composite polymer to enhance its usability (Eng *et al.*, 2017). Various forms of fillers are being added to basically improve the mechanical properties of the specimens. In one instance, the clay reinforced parts exhibited improvement in Young's modulus, but the elongation remained unaffected and also the tensile strength (Gurr *et al.*, 2008). Polly *et al.* have made a study on extrinsically self-healing photo curable polymers developed by the process of sterolithography. Microcapsule was added in the form of filler that played an important role in actuating the process of self-healing. The method has no much intricate studies with respect to optimization of process parameters. This study also indicates the ability to include microcapsules in the process of AM which enhances the various functional properties of the part (Sanders *et al.*, 2019). Peng *et al.* have made an attempt to develop polymer composite using the method of SLS without losing the properties of the material due to higher wavelength of laser. SiC polymer composite with surface modification by utilization of polyvinyl butyral (PVB) was developed and printed. Surface modification of the polymer composite helps in absorption of wavelength upto 500 nm. PVB has great impact on the properties such as agglomeration and aggregation. Addition of PVB greater than 7 wt% will not have notable effect on the results (Zhou *et al.*, 2018). A comparative study of polyamide 6 (PA 6) and PA 6 reinforced with yttrium stabilized zirconia and hectorite clay was performed using the process of SLS. Microstructure studies indicate the even distribution of filler into the matrix. The method was developed by blending of solution and later sprays drying. However, the method of spray drying has a great impact on reducing the tensile strength of the parts. This method paved the way for development of dense parts (Wahab *et al.*, 2009).

Opportunities and Challenges

Opportunities

Additive manufacturing has the great potential of growth in the near future. The changes that have taken place in last three decades, starting from the 1980s with un-commercialized knowledge to being an industry of nearly 4 billion dollar in 2014 is the exceptional path of growth. The prediction of growth of additive manufacturing industry is set to reach 21 billion dollars by 2020. The development of this segment of manufacturing is achieved through sustainability approach, reduction in lead time and

manufacturing cost, requirement for personalized and customized products and introduction of new business models (Ahuja *et al.*, 2015; Wohlers, 2014, 2015).

FDM has high potential for utilization as free form of printing with any multifarious geometry with less cost as compared to that of conventional form. The abundance of utilization of FDM has led to its use extensively in every field of manufacturing. The usage of AM technology in aerospace sector has seen reduction in product lead time by 30%–70%. Non recurring product cost was also reduced by 45% and considerable reduction was also noted in manufacture of small components (Raja *et al.*, 2006). Medical industry has been an efficient benefiter of AM technology that has helped the learning community as well as treating community. Effective pre surgical planning, tool of communication for better understanding between doctors and patients and to learn various process of surgeries can be effectively carried out with the help of AM (Dhakshyani *et al.*, 2011; Liu *et al.*, 2005; Petzold *et al.*, 1999). Architectural and jewelry domains require complex design to be developed which is a tedious task at hand of artisan. AM overcomes these deficiencies and can develop any geometry of complex shape with aesthetics.

The shift of manufacturing sector toward sustainable development according to the regulations laid by the climate governing bodies is the necessity of the hour. AM has seen leaps and bounds in its strategies to shift toward sustainable manufacturing. The necessity changes in the designed model could be easily changed and improvised through the CAD model and can be printed at a greater pace than the conventional form. The role of AM has a great role to play not only in industry but as well in education sector. Though a large arena of scope but the implementation to the real world on full scale takes its own time (Keshavamurthy *et al.*, 2019).

Challenges

There are few challenges to be solved with utilization of AM in full scale. The process parameters enact more influence on the specimen of the part than any other property. Considering from the beginning, the extrusion of filament and the accuracy of required diameter has to be seen with precision. The variation of diameter of the filament can cause numerous problems during infill composition and may cause greater difference in the raster width. Finite element method of analysis shows the uneven formation of bottom surface due to distortion in the fabricated part over temperature differences which may have caused due to less bond strength between the molecules and meso structures. Void formation due to rapid cooling decreases the properties of the composite (Chou and Zhang, 2008). The clogging of nozzle with nanocomposites could be addressed by controlling the size and distribution of the conducting particles. It was also noticed that the clogging could be overcome by maintaining the printing speed, temperature, and time (Gonzalez *et al.*, 2017). Xin Wang *et al.* have discussed the limitations of using virgin polymer and have reviewed the development of polymers with addition of filler materials. Polymer has greater properties and flexibilities but the use of this for wider application is hindered due to lack of mechanical strength and functional properties, this could be overcome by addition of certain materials as fillers and use the filament. The research for addition of filler materials either in the form of particulates, fibers or nanocomposites have been studied extensively and drawn in the form of filament. The improvement in mechanical, thermal, and electrical properties could be observed clearly. The orientation of the fibers could be greatly achieved in the required form (Wang *et al.*, 2017).

The limitations of 3D printing is just not restricted to few conditions, the hindrances have led to its narrow applications in large areas. Limitation of speed, materials, post processing, temperature fluctuations, and more of prototype building than the functional parts are few of the troubles encountered in building a part. These properties have restricted for utilization of 3D printed parts for load carrying components in structural parts and various applications. These challenges and limitations of AM have been discussed as follows.

Void

One highlighted category of limitation of AM is formation of void between the layers. The properties of the matrix and reinforcement play an important role in determining the formation of bond between two layers. The parts developed by FDM have high impact of this property which leads to delamination and reduced mechanical strength (de Jong and de Bruijn, 2013; Zareiyani and Khoshnevis, 2017). Hasti Eiliat *et al.*, in their conference paper, have studied about void formation and delamination as major setbacks for the parts developed by material extrusion process. Optimal value of raster orientation and bead width will have greater impact on reducing the void, discontinuities, and delamination. They also developed a mathematical model to demonstrate the optimal value or bead width and orientation for the 2D parts to be sliced (Eiliat and Urbanic, 2016). Paul *et al.* have made an effort to study the effect of nozzle geometry on void formation. The typical cylindrical nozzles are used in commercially available FDM printers; however, less voids were formed in the parts developed by the nozzle having rectangular geometry (Paul *et al.*, 2018). Sigmund *et al.* have raised the same concern of uncontrollable property for formation of void during the production phase. To identify the unmeasurable influence of void on various properties the authors have developed a statistical model to quantify the reduction in properties due to void. Same scale model was experimentally developed and tested. The analysis was carried out by determining the void size for transversely developed parts and was tested for tensile properties to quantify the developed model. It was established that the polymer chains and fracture mechanics plays a secondary role in determining the above process (Tronvoll *et al.*, 2018).

Production time

The process and effectiveness of production of parts in AM has great impact on time. There exists great trail difference in production time when compared to conventional process. This constraint makes the manufacturer to choose conventional mechanism as the method of preference for mass production (King, 2012). While developing a part the time is dependent mainly on the length in z-direction. The printing time of the parts independent of the process directly depends on the build height

(Gao *et al.*, 2015). Many researchers have taken up various models and methods to determine the cause and suggest the suitable remedy for the reduction of production time of the parts. Cheng *et al.* made a study assuming that production time of the time is directly proportional to the build height for SLA. Hence, the time to develop each layer was considered to be constant (Cheng *et al.*, 1995). Another group of researchers have made an effort to determine the estimation time for SLA by considering the parameters such as laser power, scan speed, spot size, and strategy of scanning. The model developed used only estimation data and not real time application (Chen and Sullivan, 1996).

Mechanical properties

Though many research activities have been carried out at the core of enhancing the mechanical properties of the AM parts, yet there remains a large hindrance in reaching or excelling the properties to those parts developed by subtractive or formative technologies. The reason for this reduction in mechanical properties may be attributed to very less availability of the materials for the particular process and unavoidable void formation between the layers in the process of FDM (Kruth *et al.*, 2007; Agarwala *et al.*, 1996). However, mechanical properties of the component are dependent on the joining boundary part of the component, which exhibits very weak bond in case of layered structure. Hence, reduction in residual stresses and anisotropic behavior of the components reduces overall mechanical property of the component (Chacon *et al.*, 2017). In depth studies show that anisotropic behavior and mechanical properties of the parts developed by FDM are found to be dependent on the process parameters and the kind of material adopted (Monzon *et al.*, 2017). The hindrance of anisotropy has great effect on lithographic process as well, which can be improved by adopting the method of post curing (Kumar and Kruth, 2010).

Biocompatibility and regulations

The advancements of AM have its utilization even in the field of medicine and food. Implementation of bio part or drug design can be accurately and precisely carried out depending on the individual data. There remains an open technological benefit for the patients to improve on the health conditions (Bibb *et al.*, 2009). However, the regulations are still in the stage of incumbency for the governing boards to have control upon. Development of weapons and other harmful drugs are to be seen in large scale by using AM technology, which has led to its full fledge utilization in many countries (Abdulhameed *et al.*, 2019). Apart from these issues there arises the complexity of emission of harmful gases like CO₂, CO, NO_x, SO_x, PM_x during the process of printing. Most of the polymer materials used in printing are biodegradable but with consistent time frame has a minimal effect of the environment (Drizo and Pegna, 2006).

Design constraints

Although the free form of design fabrication is possible through AM for development of any complex part, there remains the hindrance of complete utilization due to lifecycle cost analysis, studies of impact on the developed part, CAD software for analysis complex geometry and implications in choosing of multi material. The understanding of CAD models to larger sector such as toy manufacturers, game developers, and house wares needs to be analyzed for easy utilization. Involving new methods of manufacturing such as imbibing sensors for smooth surface finish and dimensional accuracy has still to be analyzed.

However, there arises a large scope of modifying the properties based on the desired outcomes, which enhances the end result of the component. Moreover, 3D printing has greater design flexibilities in building of complex parts and controlling the internal designs through CAD modeling without waste of materials, which is an excellent combination of process flexibility and high performance products. The emergence of this technology is now established in small scale across various industries, as the time lapses the employment of the same could be seen in every household for a mixture of applications. Aerospace and automotive sectors have already started manufacturing simple parts by the use of FDM. As the technology improves, full scale usage of FDM in these fields will be enhanced to greater extent. The medical field is seeing an exponential growth in research and fabrication of organs for implant and surgery. The norms are yet to be still established in written records of constitution for implementing use of AM in medical industry. This is paving a wide open path for exploration in many fields of science.

Case Studies

Aerospace Industry

The industry of aerospace is highly expensive when concerned to manufacture of various parts on timely basis. The adaptation of new technologies in aerospace industry, if effective, is fast. Manufacture of various parts with reduced time and to develop only a required dimension either to join or replace involves huge accounts. AM is the new technology being embraced by aerospace industry for development of low cost, light weight and lower volume arts.

Advanced Composite Structures (ACS) a renowned manufacture company for aerospace parts has emerged as a frontier in utilizing AM process for development of numerous parts. The conventional process followed by the company was utilizing lathe machines along with different tools and special equipment for manufacturing. The investment in this process was very high and certain small changes resulted in huge time involvement. The shift toward AM for tooling needs made a huge cost reduction and also any change in the design was quickly implemented without much delay. The change has positively impacted in the overall growth the company.

Piper Aircraft another renowned manufacturer uses hydro foaming parts for development of various structural parts. Aluminum was basically used as material for sheet foaming. Research studies paved a way for utilizing polycarbonate as a replacement for aluminum. The parts of structural applications are being developed by the process of FDM in which the program is written at a very short time of 10 min which was not the case in CNC, which took 4 h to program the code. The pace of manufacturing was much faster in AM than CNC without requirement of any operator in glance of manufacturing. Less than 20% of the material was seen as wastage in FDM process, used in structural support, which was very much lesser than CNC wastage (Hiemenz, 2016).

Automotive Industry

AM is no way behind in automotive sector. Spring Srl, Italy an engineering design company used the method of AM to design certain complicated customized designs. Rear mudguard of quad was designed and developed using the process of AM. The mold was developed taking into consideration the intricate designs of the part to be fixed at rear end. Required structure with proper holes for attachment to the vehicle body was carried out using Nylon 12CF through the process of FDM. Carbon was laminated over the surface for the part to be used without any further modifications. The part took 2 days and weighed 2 kg while manufactured through CNC. However, through the process of AM the lead time was reduced to 1 day and build time was only 6 h. The weight of the part was just 0.5 kg. 43% reduction in cost was seen in the part developed by AM. The improvement in customer band was seen with special solution to specified design requirement was seen (Gualdo, 2018).

Reduction in manufacturing cost of automotive car has been a large field of analysis for big manufacturers. The result of overcoming this has been seen through printing an electric car through the process of AM by Local Motors and Oak Ridge National Lab, USA. Carbon fiber reinforced plastic was used to develop this car of raw design. The average price of this AM car is around \$5000. There was reduction in the number of working parts and also reduced manufacture time along with minimal wastage.

Conclusion

The future research required for the development of 3D printing still presents a vast research field to explore. Many researchers are involved in exploring the possibilities of the improvement of the filament, machine or performance; yet, the desired properties of the filament need to be achieved to a greater extent. Post processing of the fabricated component still needs to be developed with any further addition of steps. However, it has paved the way for the designers, to develop and customize the required dimensional component of any form.

New techniques and materials are also to be examined for enabling the wider use of applications in industries as well as home needs. The law needs to be regulated strictly for protection of developed designs. The mass production of the component in a timely manner also needs further research and development. Finally, this method of manufacturing is embracing the present world scenarios in a rapid manner and with improvements in this technology the shift to its further usage is evitable to be seen in the near future.

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Properties for Polymer, Metal and Ceramic Based Composite Materials

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Introduction

Material processing dictates the resulting structure of a material which in turn defines its properties. The design and development of a material is accomplished based on this processing-structure-property relationship which forms the heart of material science and engineering (Chung, 2017a). The selection of proper material is crucial in the engineering design process as a design engineer needs to select the correct material for the best performance within the developed product design. The difficulty in selecting a material increases with an increase in the complexity of a product. It is a challenging task for a design engineer to select a suitable material from a wide range of available materials. This is because, a single material must be simultaneously capable of satisfying a set of complex design requirements and cost effective. Hence, a design engineer must have a sound knowledge of the properties of various materials to satisfy the design requirements (Sapuan, 2017a).

The advancement of human life is based on the development of products of new design, material and technology. The conventional materials, viz., metals, ceramics, woods and polymers, are largely replaced by composite materials due to light weight, corrosion resistance and part consolidation. A composite material is a mixture of two or more materials to produce a new material with new properties. Composites comprise of two or more phases separated by a distinct interface where normally the constituent materials are processed separately and then bonded. The properties of the composite materials as a whole are different from each of the constituent materials. The composite materials consist of a reinforcing phase in the forms of fibers, particles or sheets that are embedded in another constituent called matrix (Sapuan, 2017b). The load carriers (e.g., fibers, continuous strands, or particles), increase the stiffness of the composites. The composite materials can also be categorized based on the fibers' size (short, or long), or the fiber's type (synthetic, or natural). Composites, moreover, can be classified into three main categories based on the type of matrix material: metal matrix composites (MMC), ceramic matrix composites (CMC), and polymer matrix composites (PMC) (AL-Oqla and Salit, 2017). This makes possible to create a new material systems having unique properties that are impossible to obtain with a single monolithic material. Composites are widely used in aerospace industries along with various mechanical engineering applications like internal combustion engines, machine components, automobiles, mechanical components such as brakes, drive shafts, flywheels, equipment for process industries, sports and leisure equipment, ships and boats, and biomedical devices. Composites are heterogeneous materials whereas monolithic materials are often isotropic materials at first approximation with exceptions such as rolled alloys having anisotropic properties. The fiber-reinforced composites, viz., MMC, PMC, CMC, do not show significant plastic behavior like metal alloys. This does not indicate their brittleness like monolithic ceramics. Instead, they show complex failure mechanism having high toughness that can be used in numerous applications requiring durability and reliability (Zweben *et al.*, 2015).

Structure and Composition

The rapid development of modern science and technology requires special research in the field of materials through designing of materials based on the expected properties. The composite materials are made up of metals, non-metals and polymer materials through several methods that preserve the benefits of the primary components and overcome some disadvantages revealing some new properties.

Composite material is a complex multi-component system made up of matrix materials and reinforcing materials as shown in Fig. 1. In addition, some naturally-occurring materials like wood and bone are also considered to be composites. But, in the present discussion, mainly synthetic (or man-made) composites will be considered. Matrix material is a continuous phase consisting of metal matrix, inorganic non-metallic (ceramic) matrix and polymer matrix. Reinforcing material is a dispersed phase, generally made up of fibrous materials.

The fibers offer high strength and stiffness along with the opportunity to modify the material in order to match its mechanical properties with that of the loading environment. Many natural materials have fibrous structure, whereas, natural fibers possess lower strength and stiffness than man-made fibers. The higher strength and stiffness of the fibers are utilized in a monolithic composite material by binding them with a matrix material that possesses lower strength and stiffness than the fibers for numerous engineering applications. In order to improve the interfacial bonding between the fibers and the matrices and to prevent any damage by the processing equipment, the fibers are subjected to surface treatments to achieve high finish. The general surface treatment processes used are chemical sizing, surface etching by acid, coating etc. The final shape of the composite materials is given by the matrix materials that govern the parameters of the manufacturing processes. The stiffness of the matrix should be sufficient enough to provide uniform loading of fibers. Even the fracture of the weakest or damaged fiber should not damage the material. Hence, the matrix should evenly redistribute the load from the damaged fiber to the adjoining ones (Vasiliev and Morozov, 2018).

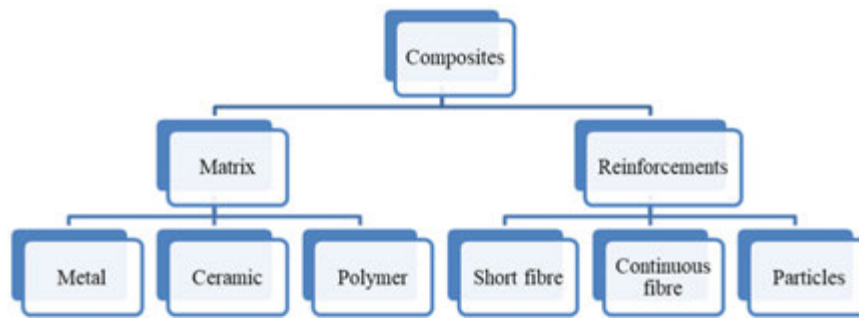


Fig. 1 Composition of composite materials.

Reinforcements

The reinforcing materials influence the strength, stiffness and density of a composite material. The reinforcements provide strength and stiffness to the composite material and usually consist of fiber or a particulate. Particulates are spherical, platelets or any other uniform or uneven geometry. Particulate composites are weaker, less rigid and less expensive compared to continuous fiber composites. The length of a fiber is larger than its diameter and its aspect ratio, i.e., ratio of length to diameter, can be varied to a great extent. The continuous fibers have long aspect ratios and a preferred orientation while discontinuous fibers have short aspect ratios and random orientation. The sheets of continuous fiber composites are stacked in different orientations to form continuous fiber composites having the desired strength and stiffness. Generally, the fibers with smaller diameters have higher strength at the expense of its cost. The smaller-diameter, high-strength fibers have greater elasticity and are more submissive to fabrication processes such as weaving or forming (Campbell, 2010).

Some typical fibers that may be continuous or discontinuous are explained below.

- (1) *Glass fibers*: The glass fibers are commercially available in a wide range of chemical compositions. The commonly used glass fiber is silica based ($\approx 50\%–60\%$ of SiO_2) that include a group of other oxides like calcium, boron, sodium, aluminum, iron etc. These oxides alter the network structure and bonding and properties like reduction in viscosity for easy processing. The silica based glasses generally have low density, high strength and not so high elastic modulus. It has high strength-to-weight ratio but moderate modulus-to-weight ratio. The glass fiber cannot withstand load for longer period due to the moisture adsorbed by the glass fiber during its processing (Chawla, 2016). Glass fibers are manufactured by pulling out of glass in molten state through orifice and nearly 200 filaments form a strand. The strands are made into roving, fabrics or mat for easy handling. The glass fibers are widely used in the field of automobile, aerospace, marine, civil construction, electrical, electronics and biomaterial.
- (2) *Carbon fibers*: Carbon fibers are the fibers that contain 90% or above carbon. They are synthesized by thermally converting low carbon organic fibers like polyacrylonitrile (PAN) consisting of thousands of filaments having a diameter between 5 and 10 μm . The carbon fibers possess high tensile strength, stiffness and chemical resistance and low density. These fibers can be used as reinforcement in polymer matrix to synthesis a composite having lightweight and improved mechanical properties. The combination of many advantageous properties like thermal, electromagnetic, electrical and chemical establishes carbon fibers as a great choice for high performance applications (Pusch and Wohlmann, 2018).
- (3) *Aramid fibers*: Aramid fibers are a type of chemical fiber synthesized from long chain synthetic polyamide where at least 85% of the amide linkages are joined directly to two aromatic rings. Kevlar and Nomex are two commercially available aramid fibers. Aramid fibers have high firmness and high resistance to stretch, chemicals and elevated temperature. Kevlar fibers are polymeric in nature having closely packed aromatic polymer chain. Their enhanced properties like high strength, toughness, stiffness and melting temperature offers enhanced structural performance that works better than steel and have half the weight fraction of steel (Alagirusamy and Das, 2011).
- (4) *Boron fibers*: In spite of having high stiffness, boron fibers possess lesser modulus than carbon fiber that restricts its applications. The boron fibers are synthesized by chemical vapor deposition of boron on to a tungsten or carbon wire of approximately 12 μm diameter that results in larger diameter boron fibers of about 100–200 μm . Boron fibers get degraded when it comes in contact with aluminum or titanium matrices as the metal matrix composites are processed at high temperature (above 500°C). Hence, the fiber surfaces are covered with a silicon carbide layer of around 5 μm thick using chemical vapor deposition technique and are known as boron carbide fibers or borsic (Vasiliev and Morozov, 2018).
- (5) *Natural fibers*: The natural fibers are used as reinforcements for polymer matrix composites. They possess high toughness, thermal properties, and biodegradable and are good insulator against heat and noise. However, they have low resistance to moisture and poor compatibility with hydrophobic polymer matrix. Some common examples of natural fibers are sisal, jute, pineapple leaf, banana stem, coir etc (Sapuan, 2017b).

Matrices

The materials that can withstand stresses and can incorporate the reinforcing forces by offering strong bonds with them are a potential material to be used as matrices. Some inorganic materials, polymers and metals can be used as matrix material in

structural composites. The two main purposes of the matrices are to hold the reinforcement phases in place and to deform itself to distribute the stresses amongst the reinforcements under an applied force. The advantages like light weight, ease of handling, moisture sensitivity, quick response to changing temperature etc. are applicable for matrices intended for a particular purpose. The different fabrication methods for composites are selected based on matrix properties and the influence of matrix on the properties of reinforcements. The classification of composites based on the matrix materials include metal matrix composites (MMCs), ceramic matrix composites (CMCs) and organic matrix composites (OMCs). The OMCs are further divided into two types as polymer matrix composites (PMCs) and carbon matrix composites.

Metal matrix composites

Metal matrix composites (MMCs) consist of fibers or particles surrounded by a matrix of metal. The MMCs possess very high stiffness and strength and its temperature resistance is superior to PMCs and pure metals. Though the MMCs possess certain other advantages like better abrasion and creep resistances, resistance to degradation by fluids, dimensional stability and non-flammability, their applications are limited because of their higher weight and cost of production. In recent years, light MMCs has been developed for various applications in automotive industries like fiber reinforced MMCs for pistons and crank cases (Park and Seo, 2011). As far as matrix is concerned, various metallic systems like Al, Be, Mg, Ti, Fe, Ni, Co, and Ag has been explored for use in MMCs. But largely aluminum matrix composites are used in various applications. From reinforcement point of view, generally ceramics are used due to its combined properties of stiffness, strength and relatively low density. The ceramic reinforcement materials include SiC, Al₂O₃, B₄C, TiC, TiB₂, graphite, and a number of other ceramics. The reinforcements materials are available in three forms, viz., continuous, chopped fiber or whiskers, and particulates (Hunt, 2000).

The MMCs are fabricated mainly through two routes, viz. liquid state fabrication and solid state fabrication. In liquid state fabrication, the dispersed phases are incorporated into a molten matrix material, followed by its solidification. The liquid state fabrication methods include stir casting, pressure less melt infiltration, pressure infiltration and disintegrated melt deposition. The solid state fabrication is a technique in which the MMCs are formed due to bonding of matrix metal and dispersed phase by virtue of mutual diffusion occurring between them in solid states at higher temperature and under pressure. The solid state fabrication includes diffusion bonding and powder metallurgy (Anish *et al.*, 2012).

Ceramic matrix composites

Ceramic matrix composites (CMCs) are made up of ceramic fibers or whiskers in a ceramic matrix. The main intention behind developing CMCs is to enhance the advantageous properties of ceramics with the addition of reinforcements and to limit their intrinsic flaws, mainly brittleness. Unlike PMCs and MMCs, CMCs are known as inverse composites as the failure strain of the matrix is lower than that of fibers that results in the failure of the matrix first. CMCs have high toughness and display a high failure stress if the fiber matrix bonding is not too weak or too strong that is achieved through the use of fiber coating referred to as the interface. Both oxide fibers (mixture of alumina and mullite) and non-oxide fibers (carbon and SiC based fibers) are used in practice. The non-oxide fibers possess lower density and better strength retention and creep resistance at high temperatures than oxide fibers (Naslain and Pomeroy, 2016).

The interphase in CMC is a thin coating (< 1 μm) deposited on the fibers or formed in-situ during composite processing. Its main function is to transfer load, deflect crack and acts as a diffusion barrier. The different types of ceramic matrices are silica-based glass ceramics, LAS, MAS, MLAS, CAS and BMAS (L = Li₂O, A = Al₂O₃, S = SiO₂, M = MgO, C = CaO, and B = BaO). Nonoxide matrices comprise mainly carbon, silicon carbide, and silicon nitride (Naslain and Pomeroy, 2016). Unlike PMCs and MMCs, CMCs cannot be processed by melting technique. They are synthesized by sintering technique that makes a blending of materials into a uniform mass by heating to high temperatures without complete melting. If continuous fibers are involved, sintering is headed by infusing the assembly of fibers with a slurry of ceramic particles dispersed in a liquid.

Polymer matrix composites

Polymer matrix composites (PMCs) or fiber reinforced plastics (FRPs) are materials that uses organic polymer as matrix and fiber as reinforcement. There are different types of PMCs according to the polymer types like thermoset and thermoplastic polymers, epoxy, polymers other than epoxy, amorphous and semi crystalline polymers (Chung, 2017b). The types of thermosets for FRPs include polyesters, epoxies and high performance thermosets, polyurethanes, silicon rubbers, phenol formaldehydes, unsaturated polyesters (UPs). Epoxy resins may also be used in conjunction with most composite processing techniques and are particularly suited to B-stage processing. Cure generally involves polyaddition with a multifunctional co-reagent, referred to as the "hardener", to produce a three-dimensional network with low shrinkage, and excellent adhesion and environmental resistance. Drawbacks of conventional resins include somewhat higher viscosities than for UPs, long cure times, and moisture uptake. Both semi crystalline and amorphous glassy polymers form viscous melts that need to be processed at temperatures well above the glass transition temperature, T_g. However, because semi crystalline polymers melt well above T_g, it is the melting point, T_m, that defines the processing window. Semicrystalline thermoplastics are tough and resistant to organic solvents, but many inexpensive and easy-to-process low T_g polymers, such as polyethylene, also show poor adhesion owing to their lack of functionality, and low softening temperatures, often associated with excessive creep. A good compromise between cost and performance is provided by polypropylene (PP, T_m170 °C), for which functionalized additives are available to improve adhesion. Aromatic high-performance amorphous thermoplastics such as poly (ether sulfone) (PES, T_g230 °C) or poly (ether imide) (PEI, T_g215 °C) have also

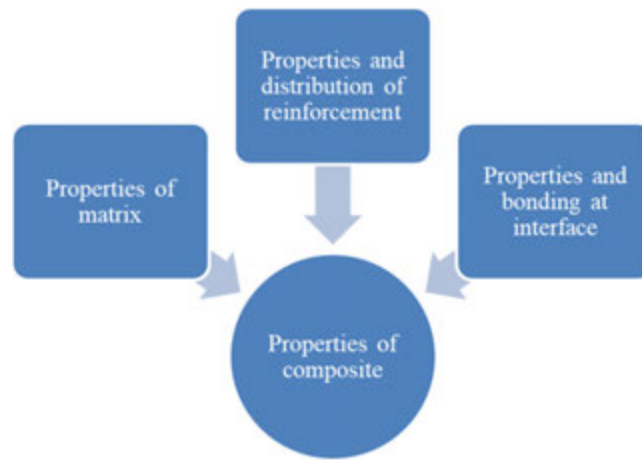


Fig. 2 Influencing factors for properties of composites.

attracted interest as advanced FRP matrix materials. They are less expensive than PEEK and tougher than thermosets, but there remain concerns over their solvent resistance (Plummer *et al.*, 2016).

Properties of Composite Materials

The properties of a composite material depend on (1) the properties of the constituent materials, (2) the size, shape, amount and pattern of distribution of reinforcements and (3) the efficiency of bonding between the matrix and reinforcement in transferring stress across the interface as shown in Fig. 2.

Mechanical Properties

The engineering materials should possess certain strength, modulus and other mechanical properties for various successful applications. The mechanical properties of composite materials largely depend on the performance and arrangement of reinforcing fibers. In order to achieve a greater difference in mechanical anisotropy of composite materials, the reinforced fibers are arranged in different ways. The unidirectional composite materials in which all the fibers are arranged in parallel in the same direction higher strength appears along the fiber direction whereas it decreases significantly in other directions. The combined properties of the reinforced fibers and the matrix dictates the mechanical properties of the composites. Under the influence of external load, the reinforced materials play a key role as load bearers and the matrix transfers shear stress amongst the fibers and prevent them from buckling. For instance, glass fibers having high axial load bearing capacity are introduced into matrix to increase the tensile strength of the synthesized composites to a large extent (Wang *et al.*, 2011a).

Impact

The composite materials must be capable of withstanding impact load for various applications. At times, little impact energy can severely reduce the static strength of composite materials, influencing component reliability. Likewise, sometimes an effort to enhance the tensile strength would lead to the decrease of impact property simultaneously. Amongst the composite materials, the fiberglass and Kevlar fiber composites possess high impact property whereas carbon fiber composites used in structures possess low impact property. The impact toughness is measured by calculating the amount of energy required to breakdown a specimen (Wang *et al.*, 2011b).

The wide use of composite materials is restricted due to the damage generated by the induced impact load. This damage needs to be investigated for the structural performance of the composites under impact loading. The failure mechanisms can be divided into: (1) breakdown of matrix and debonding in fiber/matrix interface due to high transverse shear stresses in the top layers; (2) transverse bending crack due to high flexural stresses in the bottom layers; (3) interlaminar delamination due to cracks restricted and diverted through the interlaminar area; (4) fiber failure damage mode under tension and fiber micro-buckling under compression loading and (5) penetration (Jefferson Andrew *et al.*, 2019).

Fatigue

The study of fatigue mechanism is very much important to assess the durability and integrity of various materials for different applications. The inhomogeneous and isotropic nature of composite materials play a key role in damages occurring in them. The damage in composite materials occurs globally and is different from that of metal where damage occurs in a localized manner, i.e., a single crack leads to complete failure. In composite materials, the damage first initiates within the matrix material (cohesion) or at the interface between the matrix and the fiber (adhesion). Generally, the fatigue failure in composites starts as transverse ply cracking at free

edges or at notches as this fracture mode has the lowest resistance. The cracking of matrix within the composite materials is described by correlation between the fracture toughness of the matrix to quasistatic and fatigue performance of the composites that reveals the significant influence of microscopic geometry. The ability to take up induced deformation by the matrix decreases with increase in volume fraction of the fibers as less matrix material is present between the fibers (Alderliesten, 2013).

Tribological Properties

The different polymers and polymer composites are well suited for engineering applications having some critical problems like wear and friction. Initially, attention was focused on studying the tribology of metal-metal and metal-ceramic contacts. However, at present, more attention is converged towards investigating metal-polymer and polymer-polymer tribo-contacts. This is because metals in structures, housings, bearings etc., are largely replaced by polymers due to their beneficial properties like light weight, cheaper and corrosion resistance. The polymer-metal contacts do not follow the general laws of friction that are used for tribology of metal and ceramic contacts that are in relative motion. The reasons for this include relative softness of polymers compared to metals, their much lower thermal conductivities that leads to heat generation in contacts and also much lower melting points. Hence, polymers cannot be used in applications of rolling, sliding or bearing components if these problems are not fixed (Friedrich, 2018).

The friction and wear properties of polymers can be improved by lowering adhesion and increasing stiffness and strength with the introduction of special fillers. The adhesion can be reduced by incorporating internal lubricants such as polytetrafluoroethylene (PTFE) or graphite. These lubricants form a transfer film on the surface of the counterpart material to reduce friction. The stiffness and strength of the polymer composites can be increased by inserting continuous or short aramid, carbon or glass fiber into the polymer matrix. It is necessary to use a high temperature resistant polymer matrix in order to overcome the high temperature generated due to sliding friction between the two mating surfaces. A change in tribological properties of the polymer composites can also be achieved by using thermally conductive fillers, including nano sized particles or carbon nano tubes. However, a reduction both coefficient of friction and wear rate can be achieved by using a mixture of nanofillers in conjunction with traditional tribo-fillers (Friedrich, 2018) as shown in Fig. 3.

The incorporation of ceramic or metallic reinforcements into the ceramic matrix such as alumina, silicon nitride, silicon carbide, glass or carbon, improves the mechanical and tribological properties of ceramic matrix composites. Ceramics possess good wear and high temperature resistant properties. However, its application is limited due to the poor friction performance. The alumina matrix in combination with silicon carbide whiskers together reduces the brittle wear rate as silicon carbide whiskers act as a mechanical barrier in the direction of crack propagation. The matrix microstructure, types of reinforcements, the bonding between the matrix and the reinforcements, experimental conditions and the processing technique of the ceramic matrix composites greatly influences their tribological behaviors. Cermets, which is a combination of ceramics (hard phase) and metals (soft phase), possess both hardness and ductility. The formation of crack within the ceramic cannot be propagated to the adjacent grains due to the presence of ductile metallic phase. In cermets, the wear rate decreases linearly with an increase in hardness that indicates the metallic behavior of cermets at tribocontacts. The main mechanism of material removal in cermets is abrasive wear (Sahoo and Davim, 2013).

Ceramic-ceramic contacts exhibit low friction due to the presence of oxide films that reduces the real area of contact. The wear of metallic counterface of ceramic-metal contacts will be low in case of soft ceramics in comparison to harder ceramics. Polymer-ceramic contacts possess low friction coefficient and wear rate compared to polymer-metal contacts. The refinement in microstructures of nanocomposites will lead to better wear resistance (Sahoo and Davim, 2013). Bioceramics for the applications of dentures and repair of teeth, bone replacement etc., should exhibit good tribological performance in biological environment. The advanced composite materials in combination with polymers, metals and ceramics can be suitably used as artificial biomaterials. The polymer biomaterials are preferred over metallic and ceramic biomaterials due to their unresponsiveness, biodegradability, high toughness, low density, low friction coefficient and ease of synthesis. The low mechanical strength and tribological properties of such polymer biomaterials can be enhanced by including suitable fillers and additives (Sharma *et al.*, 2017).

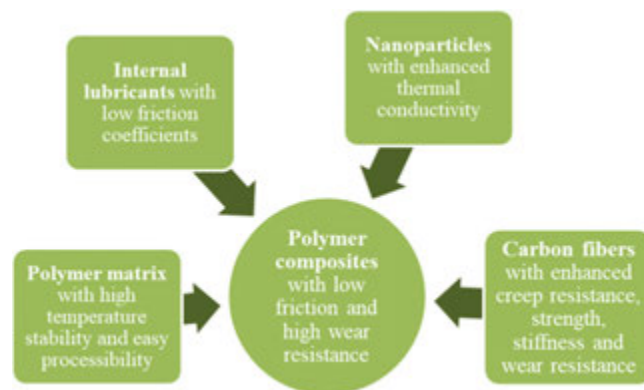


Fig. 3 Composition of polymer composites with low friction and wear.

Electrical and Thermal Properties

The polymer matrix composites filled with continuous or discontinuous fibers can be used for electronic packaging and thermal management. The continuous fiber composites are used as substrates, heat sinks and enclosures. The discontinuous fiber composites are used for die attach, electrically or thermally conducting additives, encapsulations, thermal interface materials and electrical interconnections. The continuous fiber composites possess lower thermal expansion and higher conductivity than discontinuous fiber composites. Composites possessing thermoplastic matrices have the advantage of reworking in contrast to the thermosetting matrices. The composites can be electrically conducting or insulating depending on the presence of conducting or insulating fibers. A composite can be both electrically and thermally conducting due to the incorporation of metal or graphite fibers. Whereas, it can be electrically insulating and thermally conducting due to the insertion of diamond, aluminum nitride, boron nitride or alumina fibers. For heat sinks and enclosures, conducting fibers like carbon fibers are used to enhance thermal conductivity and the ability to shield electromagnetic interference. The conductivity of composite materials increases with an increase in connectivity and volume fraction of the fibers. In order to increase the volume fraction of the fibers, a polymer having low viscosity and good wettability of fibers by matrix are desired. There exists a difference in thermal expansion coefficient between the fiber and the matrix and thermal stress during fabrication of composites occur due to its fabrication at high temperature. The fibers undergo compression on cooling due to high thermal expansion coefficients of polymers. The compression tightens the fiber-matrix interface, in spite of the degradation of performance and durability of composites on account of compressive stress in fiber and tensile stress in matrix (Chung, 2003).

Controlled resistivity ceramics, like alumina matrix composites, containing electrically conducting fibers can be used as substrates for semiconductor wafers. They can also be used as charge dissipative coatings to enhance the breakdown voltage of high power, high vacuum devices. Controlled resistivity composite materials consist of an electrically insulating matrix and electrically conducting discontinuous particulates or fibers. The higher the fiber content, the lower is the resistivity of the composite. With an increase in particulate or fiber content in the ceramic matrix composites, the dielectric constant increases and the resistivity decreases.

Metals possess high thermal and electrical conductivity due to the presence of free electrons. However, a critical situation arises when there is an additional requirement of good mechanical properties along with high thermal conductivities as conventional strengthening by alloying may lead to sharp reduction in conductivities. Thus, MMCs have a good control over the achievement of combination of properties. The conductivity of an MMC system consisting of relatively poor conducting metals like titanium can be enhanced by introducing suitable reinforcements. The possible reinforcement for enhancement of electrical conduction should be another metal. But for thermal conduction enhancement, a ceramic reinforcement having higher conductivity than matrix should be used. A thorough examination of such cases is important as the thermal conduction in ceramics usually occurs via phonons, so that heat transfer across the interface may include a change in the type of carrier. Several situations may arise in which MMCs with low conductivities are attractive, as there are certain situations in which thermal insulation, or a particular combination of electrical and thermal properties, are desirable (Clyne, 2018).

Summary

The maximum benefit of composite materials is achieved from the beneficial properties of a strong bond between the harder reinforcements usually fibers or particles and the relatively weaker matrix. Good bonding between the fibers and the matrix is possible when good wettability of the fibers and absence of porosity is achieved. The composite materials possess high strength-to-weight ratio and there is a scope of design flexibility as the composites can be molded into complex shapes. The different type of composite materials are metal matrix, ceramic matrix and polymer matrix composites based on the types of matrix used. Based on the type of reinforcements, composites materials include carbon-reinforced fiber plastic, glass fiber-reinforced aluminum, composites with carbon nanotubes, and many more.

In order to achieve high strength of the composite materials, the particles of the dispersed phase should be extremely small that will inhibit dislocation motion. In case of fiber reinforced composite materials, the applied load gets transmitted to and amongst the fibers via the matrix phase. The mechanical properties of continuous and aligned fiber composites are highly anisotropic. The strength is maximum in the direction of alignment of the reinforcement and it is minimum in a direction perpendicular to the alignment of reinforcement. The composite materials have a wide range of engineering applications for example in the domains of aeronautical, wind energy, automobile, shipping and domestic goods.

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Fundamentals of Spark Plasma Sintering for Metallic, Ceramic, and Polymer Matrix Composites Production

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Introduction

The consolidation of the powder materials at a temperature lower than their melting point is called the sintering process (Cavaliere, 2019). This process could be performed by several methods such as conventional sintering, microwave sintering, hot pressing (HP), hot isostatic pressing (HIP), and spark plasma sintering (SPS). Among the mentioned routes, SPS is the most modern, high-tech, effective, and high-speed process. The sintering procedure during SPS is similar to HP with some differences in the heating procedure of the sintered materials. The heating during HP is supplied by an external source; however, in SPS, there are both internal and external sources using a pulsed direct current (DC) through the powders and graphite die. Therefore, spark plasma, i.e., electric discharge, is produced as the result of the pulsed DC, so the heating is applied from both inside and outside of the powder compact. Moreover, like HP, SPS is an under pressure sintering process, in which an uniaxial pressure is used (Cavaliere *et al.*, 2019).

Unlike the clear sintering mechanisms during the conventional sintering process, the sintering mechanisms which are participating in SPS are still being debated and are under investigation. The most popular theory for physical modeling of the SPS process is the micro-spark/plasma model. This theory is based on electrical spark discharge between the gap of the particles. This phenomenon contains ultra-high discharged energy which is caused by low-voltage pulse current. Consequently, a local high temperature is generated at a fine contact area of the particles leading to the melting and vaporization of particle surface. Gradually, necks form between the particles in their contact areas. With the necks formation, plastic flow occurs between the particles during the sintering process that leads to the consolidation of the powder materials up to 99% of theoretical density. Furthermore, due to the generation of the high temperature, for a fraction of a second, mainly on the surface of the particles, heating and cooling rate are high during the sintering process in SPS and so the microstructure of the sintered material is more controllable. Thus, coarsening and grain growth are limited and also, fine grained materials from nanopowders could be produced, which is mostly uncontrollable in the conventional sintering process. Therefore, materials with enhanced physicomechanical properties could be produced (Munir *et al.*, 2011; Omori, 2000).

Utilization of the electrical current in the material sintering process was first implemented in 1930, which was later the basis of the SPS process. However, the commercialized development of the process was delayed until 1980. Afterward, development laboratories had begun to use it as a sintering process, especially in Japan. The first industrial system of the SPS process was introduced by Sumitomo Heavy Industries (Tokyo, Japan) in 1990, after this, the SPS and electrical assisted sintering processes usage for industrial applications have gained a lot of attention (Tokita, 2013).

From the fundamental point of view, in the SPS process, the sintering is performed by electrical current passing through the powders which are compacted under an applied uniaxial pressure; however, various factors could affect the sintering conditions of the process such as powders particle size, sintering atmosphere, sintering temperature, etc. Nevertheless, the most influential parameters could be introduced as the effect of heating rate, temperature, and pressure. As these three parameters are applied simultaneously, specifying the most effective one between them is trivial to determine and may change depending on the materials being processed (Munir *et al.*, 2006). Thus, the contribution of each parameter is delineated in the next sections.

Over the past three decades, the SPS process has attained considerable interest between not only academic researchers, but also in the production of industrial components, especially, in the manufacturing of the powder dependent products. Several kinds of materials were produced by the SPS process including metals and their alloys, ceramics, and even polymer matrix composite materials. Moreover, the new generation of advanced materials production such as nanostructured materials, nanocomposites, functionally graded materials (FGMs), biomaterials, and thermo-electric semiconductors with homogeneous high densities are possible by using of the SPS process. The SPS apparatus developments are progressing from academic and R&D levels to industrial products in the domains of automotive, cutting tool, and electronic industries (Tokita, 2014).

SPS Historical Background

The use of electric currents to sinter powder materials was studied in Germany around 1910. The use of resistance sintering method for metal sheet was patented officially by Taylor (1933) in USA. Primarily, the first generation of the SPS process was invented and patented in Japan as “spark sintering (SS)” in 1962 by Kiyoshi Inoue of Japax Inc. (Inoue, 1966, 1962). The second generation was introduced by Inoue-Japax Research Inc. as “plasma-activated sintering (PAS)” in 1986. However, the SPS process was produced by Sumitomo Coal Mining Co., Ltd (Japan) in 1989, with the expiring of the Inoue patents, which was the third

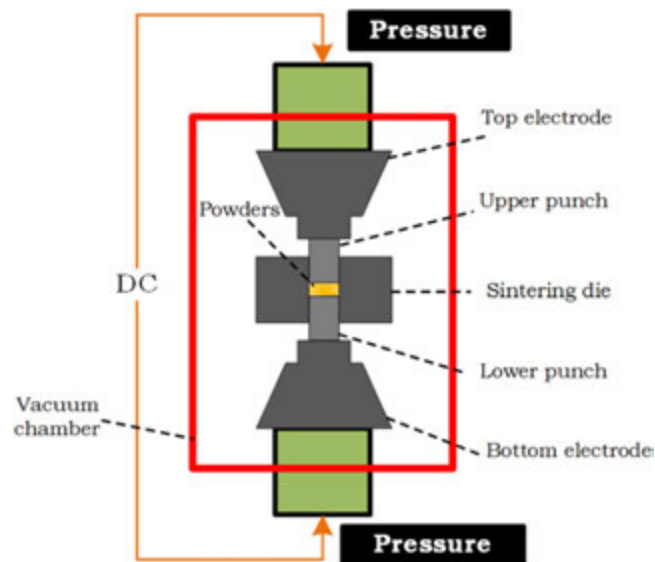


Fig. 1 Schematic of the SPS process.

generation of this type equipment. The industrialization, expanding of application, and a basic production type of SPS occurred during the fourth generation of the SPS process from 2001 to 2009. In this period of time, the SPS process replaced traditionally used processes in powder-based industrial productions, and as a result, the product fabrication was developed from medium to mass-production. Also, SPS was used not only for the sintering of materials but in the solid-state diffusion joining, surface modifier, and synthesis of the single-crystal. After 2010, in the fifth generation, the SPS apparatus was more customized with a practical manufacturing area, which is called “advanced SPS” (Olevsky, 2018; Olevsky and Dudina, 2018; Tokita, 2013).

SPS Process Principles

Apparatus and Sintering Stages

Fig. 1 shows the schematic of the SPS process. As can be seen, the system consists of two upper and lower electrodes and punches which transfer the applied pressure and pulsed DC to the powder materials that are loaded to the graphite die. The heating and consolidation processes are done in the sintering die. Due to the absence of joule heating in the sintering of nonconductive materials, the heating of the material is dependent on the pulsed DC transferring by the die to the particles, therefore, the die must be made from high-quality materials (Guillon *et al.*, 2014). To adjust the process atmosphere, the system contains a vacuum chamber, thus the process could be done in a vacuum or in the presence of an inert gas. The profile of the parameters involved in the SPS process during its sintering stages is shown in **Fig. 2**. The sintering process in SPS contains three main stages. From the starting point of the process to the sintering temperature is called the sintering stage. By the changing of the temperature, pulsed DC and displacement rates are high in this stage; however, the pressure is typically held on its initially applied value. Removing of the residual gases, rearrangement of the particles, spark plasma generation, removing impurities from the surface of the particles, softening and melting of the particles surface, formation of the necks, growth of the necks, plastic deformation, and finally sintering are done in this stage. Generally, by reaching the process temperature to the sintering temperature, the applied pressure increased to the sintering pressure and the final compaction stage starts. This stage lasts for the expected time depends on the sintering materials and conditions. During this stage, not only the residual porosities are reduced to the lowest levels, but also the particles are joined together and the near full-dense part is produced. Finally, the process is ended by starting of the cooling stage (Cavaliere *et al.*, 2017; Diouf and Molinari, 2012).

SPS Mechanisms

Although many of the research works aimed to study the sintering mechanism of the SPS process in the past decades, the effect of the applied pulsed DC on the spark/plasma generation and its effects on the sintering mechanisms of the SPS process is principally unclear (Tokita, 2013). One of the most basic offered ideas on the SPS mechanisms is based on pulsed (ON/OFF) DC which occurs as follows:

- (1) Generation of Spark plasma
- (2) Pressure impact of spark
- (3) Joule heating
- (4) Effect of electrical field diffusion

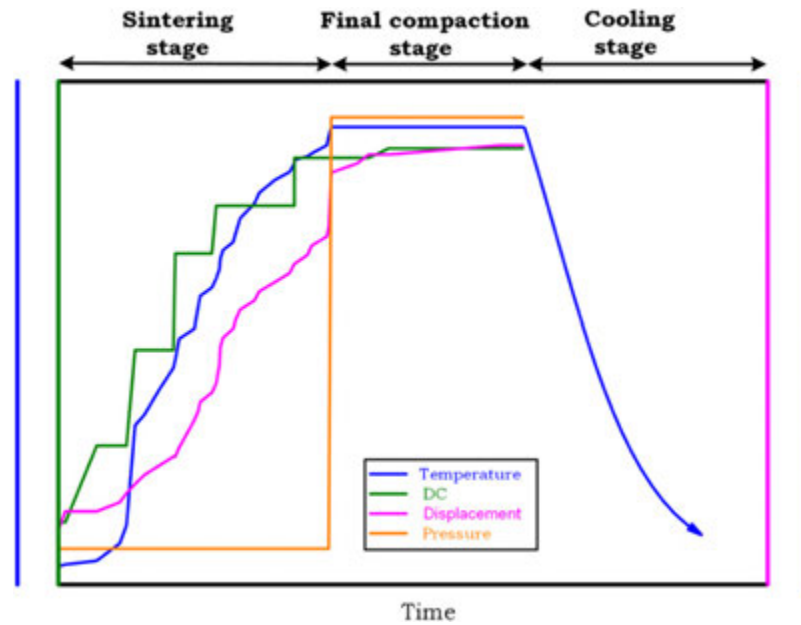


Fig. 2 Typical operating profile of the SPS apparatus.

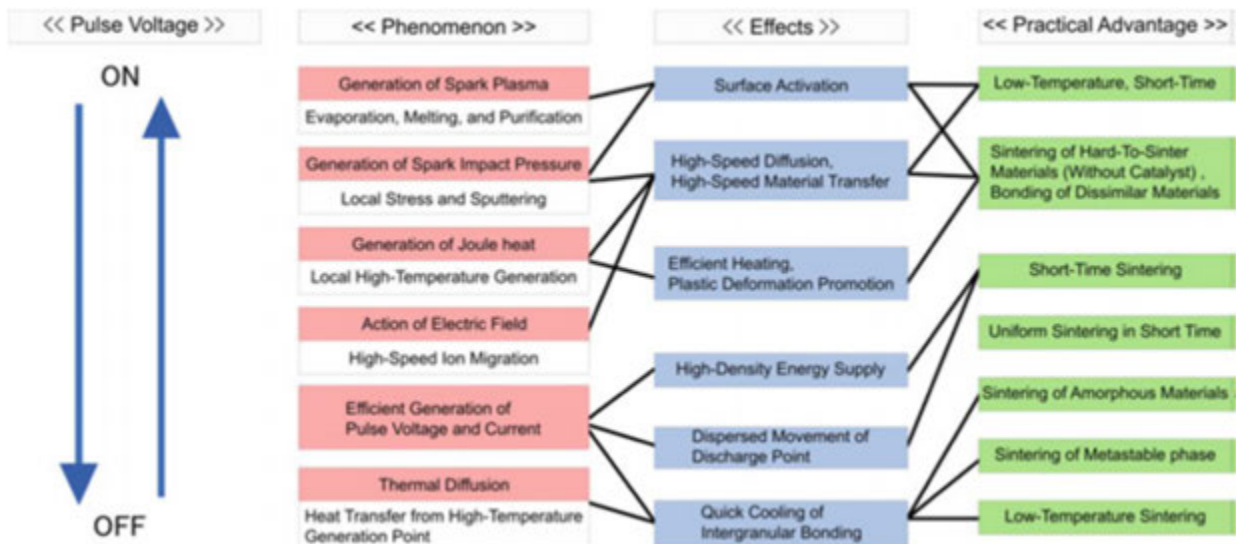


Fig. 3 ON-OFF DC effects. Reproduced from Cavaliere, P., Sadeghi, B., Shabani, A., 2019. Spark plasma sintering: Process fundamentals. In: Spark Plasma Sintering of Materials. Cham: Springer International Publishing, pp. 3–20.

The spark plasma generates high temperature sputtering phenomenon and the spark impact pressure facilitates the purifying and activating of the particles surface by removing the remaining adsorptive residual gases and impurities like oxides on powders. The electrical current generates high-speed ions which cause high-speed diffusion as the result of ions emigration (Suarez *et al.*, 2013; Tokita, 2013). More details are shown in Fig. 3.

The particle surfaces purification and activation are easier in the SPS process compared to the conventional electrical-based processes. As the result, both macro- and micro-level mass transferring are encouraged; thus, the near-full dense consolidated material with high quality is produced by the SPS process at lower temperature and shorter sintering time than the conventional sintering process. Fig. 4 illustrates the passing directions of the pulsed DC in the SPS process. As soon as the spark discharge emerges in a gap or contact areas between the powder particles, a local high temperature area (discharge column) of several to 10,000°C is generated for a fraction of second. Consequently, evaporation and melting of impurities and also particles surface happen and thus, the pulsed ON and OF time causes electron current and generation of vacuum, respectively, which initiates the absorption of the melted points toward each other and finally, necks formation accelerate around the contact points of the

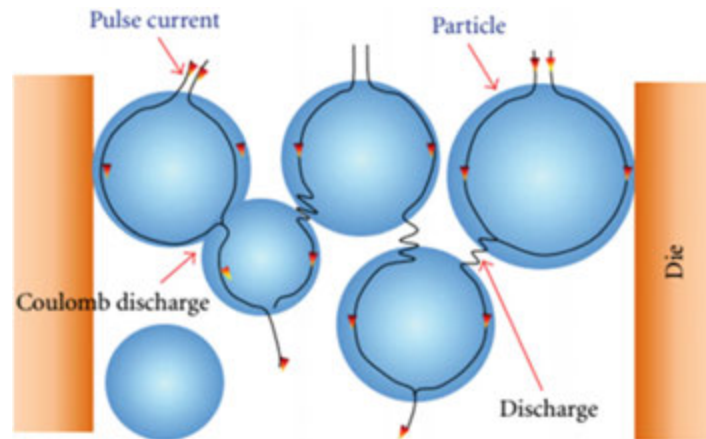


Fig. 4 Pulsed DC passing direction in the SPS process. Reproduced from Saheb, N., Iqbal, Z., Khalil, A., *et al.*, 2012. Spark plasma sintering of metals and metal matrix nanocomposites: A review. *J. Nanomater.* 2012, 1–13.

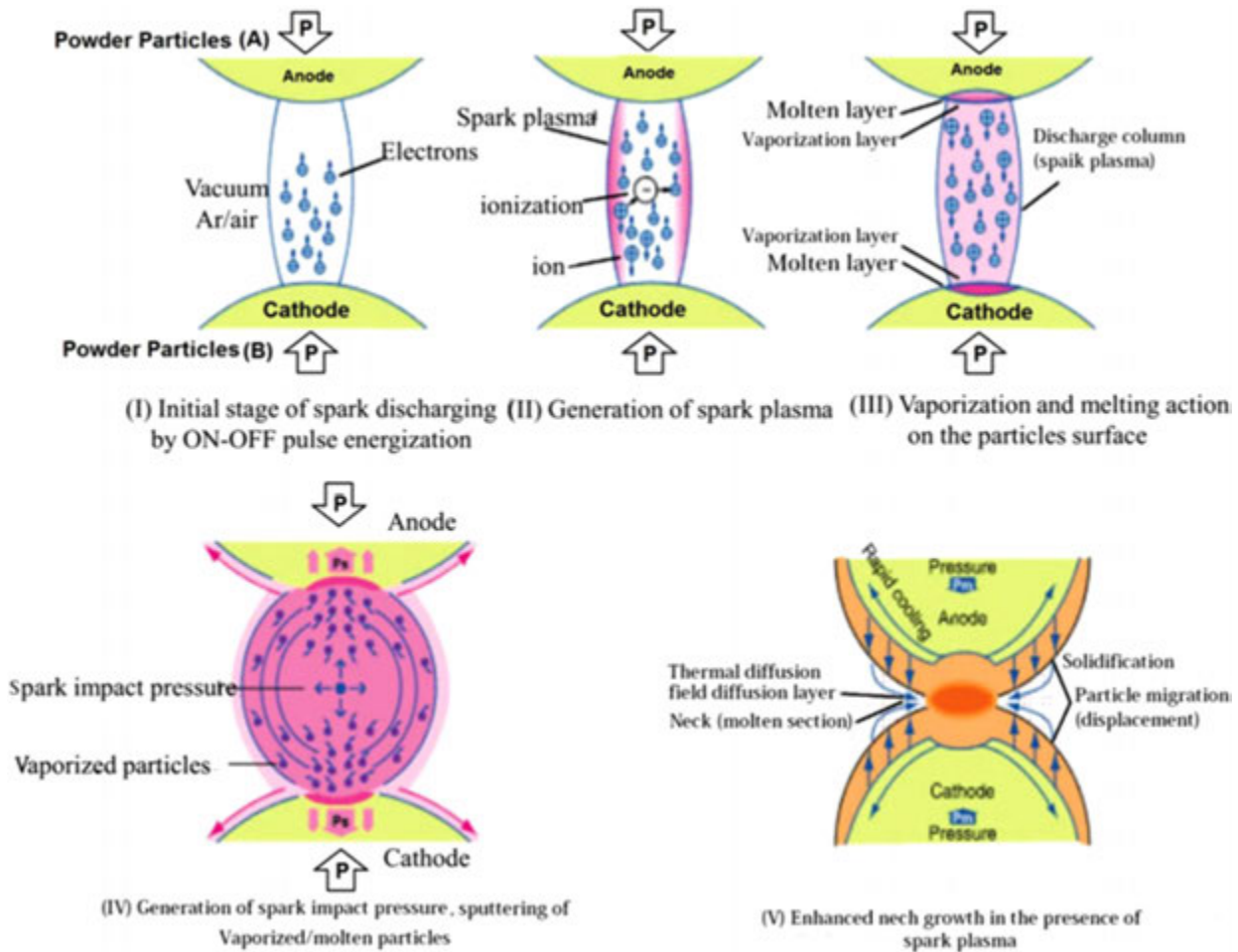


Fig. 5 Neck formation basic mechanisms involved in SPS. Reproduced from Cavaliere, P., Sadeghi, B., Shabani, A., 2019. Spark Plasma Sintering: process Fundamentals. In: *spark Plasma Sintering of Materials*, pp. 3–20. Cham: Springer International Publishing.

particles. Fig. 5 shows the different neck formation mechanisms involved in the SPS process. It is well known that a thick layer of oxide forms on the surface of the metal particles. At the initial stage of the sintering, the electrical conductivity of the powders will be influenced by the thickness of the oxide, applied pressure, and particle size. Better interaction in the contact area of the particles as the result of applied compressive pressure encourages the existing consolidation mechanism or activate the new sintering

mechanism like plastic deformation and grain boundary sliding. Moreover, the mass migration or atom transformation to the necks is facilitated by high temperature and electrical potential. The mechanisms involved in mass migration for the formation of necks are evaporation, grain boundary, surface, and volume diffusion which are active on contact points. It should be noted that during the initial step of the sintering stage the compact shrinking and necking are the lowest (2–3% of total). In contrast, the highest porosity reduction and consolidation happen at intermediate steps of the sintering stage with 92% of total densification. During this stage, the most active mechanisms are volume densification, grain boundary diffusion, and probably dislocation climb. With progressing the sintering process, the segregation of pores from each other happens during the final compaction stage. Typically, most of the segregated pores located between two or three particles with a spherical shape. Final consolidation takes place by removal of the spherical shape pores with help of diffusion. As the final compaction stage is controlled by the diffusion phenomenon, the densification speed during this stage is slow. However, by applying compressive pressure, new additional mechanisms based on grain sliding such as plastic deformation, dislocation, and diffusional creep are activated and promoted the densification process thanks to the removal of the segregated pores (Munir *et al.*, 2011; Song *et al.*, 2013; Suarez *et al.*, 2013; Zhang *et al.*, 2014).

SPS of Different Types of Materials

A large number of the research works have performed on the utilization of electric current-assisted methods for the sintering of the metallic/non-metallic materials over the past three decades. Therefore, the number of publications in this area has increased enormously since the late 1990s (Sharma *et al.*, 2019). During this time of period, the powders of the materials that were consolidated by the SPS process could be classified into four main categories: metal-based materials, ceramic-based materials, polymer-based materials, and other new generation of materials. Metal-based materials contain pure metals, metal alloys, metal matrix (nano)composites. The oxides, carbides, nitrides, borides, cement, and ceramic matrix (nano)composites classify in ceramic-based materials. Most recently, the polymer-based materials and (nano)composites, as well as other new materials like intermetallic compounds and high entropy alloys were produced by the SPS process. Here we will focus on the properties of the metallic, ceramic, and polymer matrix (nano)composites fabricated by the SPS process as a function of involving parameters.

Metal Matrix Composites

Al, Cu, Mg, Ni, Ti, and Fe are the most utilized materials as composite structures. Between them, lightweight Al, Mg, and Ti as well as Cu and Ni based composites have gained considerable attention over few past decades due to their applications in automotive, aerospace, and electronic industries. Several kinds of materials like hard ceramic particles such as TiB_2 , SiC , Al_2O_3 , B_4C , TiC , TiN , as well as sp^2 nanocarbonous materials like carbon nanotube (CNT) and graphene have utilized as reinforcements of metal matrix composites refer to the composite applications. The powder metallurgy (PM) was the most preferable method for the production of the metal matrix composites; therefore, the sintering of the produced composite powders is an important issue. Recently, the SPS process was the most used sintering method of composite materials. Here, the effects of the SPS process parameters on the microstructure and physical as well as mechanical properties of the metal matrix (nano) composites are considered.

Sadeghian *et al.* (2011) fabricated Al– TiB_2 composites by mechanical alloying (MA) of the pure Al, Ti, and B elements followed by SPS and hot extrusion processes. The sintering process was carried out at DC of 6000 A and voltage of 10 V. The sintering temperature, holding time, and pressure were 550°C, 10 min, and 35 MPa, respectively. The grain growth and particle coarsening were limited against thermal treatments of Al-20 TiB_2 nanocomposites. Also, the higher improvements of mechanical properties (hardness, yield, and tensile strength: 180 VHN, 480 MPa, and 540 MPa, respectively) were reported for the produced nanocomposite compared to composites prepared by other methods with the same material composition. Li *et al.* (2016) reported the production of the Al 5083 matrix nanocomposites reinforced by 5% TiB_2 nanoparticle via the cryomilling and SPS processes. The Al 5083/5% TiB_2 nanocomposite powders were heated to 450°C with a heating rate of 100°C min^{-1} and held on that temperature for 3 min under a pressure of 88 MPa. The produced nanocomposite showed a nanostructure with an average grain size of 74 nm. Also, compressive strength, hardness, and elastic modulus were improved from 670 MPa, 2.3 GPa, and 82 GPa for unreinforced Al5083 to 817 MPa, 3 GPa, and 86 GPa for Al 5083/5% TiB_2 nanocomposite with the same producing process, respectively, with 20% improvement of the compressive strength and 30% improvement of the hardness.

Generally, the SPS process is the main sintering process of the metal-CNT nanocomposites produced by powder metallurgy. Especially, in the case of Al matrix nanocomposites reinforced by CNT, thanks to the formation of the harmful Al_4C_3 phase during conventional sintering processes. SPS has become the main sintering process due to the lower sintering temperature and shorter sintering time which limited this brittle phase (Al_4C_3) formation (Azarniya *et al.*, 2017).

Sadeghi *et al.* (2018b) were investigated the effect of processing parameters on the microstructural and mechanical properties of the Al–CNT nanocomposites, which were fabricated by the MA and SPS process. The powders were sintered under variable SPS parameters: temperature (400–550°C), pressure (30–50 MPa), and heating rate (50–200°C min^{-1}). The results showed that by increasing of the heating rate from 50 to 100°C min^{-1} , under constant temperature (500°C) and pressure (50 MPa), the elongation and hardness were improved for pure Al, Al-0.5CNT, and Al-1CNT, however, they were decreased for heating rates of higher than 100°C min^{-1} . The relative density, hardness, yield strength, tensile strength, and elongation of the nanocomposites are

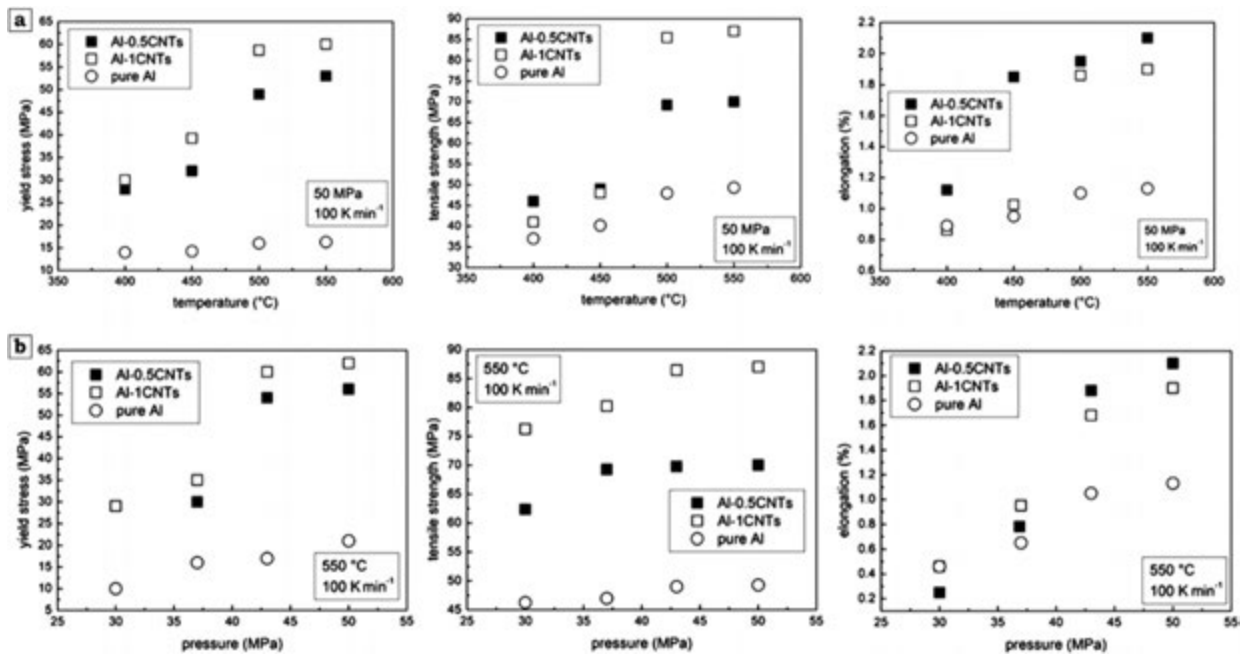


Fig. 6 The variation of yield strength, tensile strength, and elongation of pure Al and Al-CNT nanocomposites as a function of sintering temperature and applied pressure. Reproduced from Sadeghi, B., Shamanian, M., Cavaliere, P., Ashrafzadeh, F., 2018b. Effect of processing parameters on the microstructural and mechanical properties of aluminum-carbon nanotube composites produced by spark plasma sintering. *Int. J. Mater. Res.* 109, 900–909.

increased by increasing the sintering temperature from 400°C to 550°C for constant maximum applied pressure and heating rates of 50 MPa and 100°C min⁻¹, respectively. The same trend of improvement in mechanical properties observed for applied pressure varying from 30 MPa to 50 MPa with a heating rate of 100°C min⁻¹ and sintering temperature of 550°C. The changing of yield strength, tensile strength, and elongation of pure Al and Al-CNT nanocomposites as a function of sintering temperature and applied pressure are shown in Fig. 6.

Singh *et al.* (2019) investigated the effect of applied pressure of the SPS process on the densification behavior and mechanical properties of the Al-0.5%CNT nanocomposite. The produced nanocomposite powders via a combination of the PM method were sintered at a constant temperature of 500°C, holding time of 20 min, and varying pressures of 30, 50, and 80 MPa. By increasing the applied pressure, the crystallite size and relative density were increased. Fig. 7 shows the SEM images of the nanocomposite for applied pressures of 30, 50, and 80 MPa and micro x-ray computed tomography (CT) results for the 3D distribution of the porosities available in the nanocomposite structure. As shown in Fig. 7, the porosities of the nanocomposite were reduced by increasing the applied pressure from 30 MPa to 80 MPa. The higher applied pressure lead to the higher mechanical properties of the nanocomposite; thus, the compressive strength and microhardness of the nanocomposite were improved 30% and 13%, respectively, when the pressure was increased from 30 MPa to 80 MPa. In another research, they investigated the effect of heating rate and sintering temperature of the SPS process on properties of the Al-MWCNT nanocomposites, too (Singh *et al.*, 2018). The nanocomposites were sintered at various sintering temperatures (400–600°C) and heating rates (25–100°C min⁻¹) with constant pressure and holding time of 80 MPa and 20 min, respectively. By increasing the sintering temperature from 400°C to 600°C, the crystallite size and relative density increased 85% and 13%, respectively; in contrast by increasing the heating rate from 25°C min⁻¹ to 100°C min⁻¹, the crystallite size and relative density were reduced, which is in contrary with Sadeghi *et al.* report (Sadeghi *et al.*, 2018b). The highest microhardness and elastic modulus were achieved at a heating rate of the 50°C min⁻¹ and sintering temperature of 600°C.

Ujah *et al.* (2019) produced Al-CNT-Nb nanocomposites with the MA and SPS process. They had investigated the optimization of the SPS process parameters (temperature, pressure, holding time, and heating rate) on microstructure, microhardness, and density of the nanocomposites using the Taguchi method. Variations of the SPS parameters for temperature, pressure, heating rate, and holding time were 550, 600, and 630°C, 20, 30, and 50 MPa, 50, 100, and 200°C min⁻¹, and 5, 10, and 15 min, respectively. The highest value of relative density (99.3%) and hardness (38.57 HV) was achieved in optimal SPS parameters of 630°C, 30 MPa, 10 min, and 200°C min⁻¹ as sintering temperature, pressure, holding time, and heating rate, respectively.

The effect of heating rate, sintering temperature, and pressure of the SPS process on the microstructural and mechanical properties of Al-SiO₂ nanocomposites was studied by Sadeghi *et al.* (2018a). The heating rate, temperature, and pressure varied from 50–200°C min⁻¹, 400–550°C, and 30–50 MPa, respectively. As same as Al-CNT nanocomposites (Sadeghi *et al.*, 2018b), elongation and hardness were increased by increasing the heating rate from 50°C min⁻¹ to 100°C min⁻¹, after then, they were dropped sharply to the lower values. This tendency could be attributed to the effect of the heating rate on the sintering

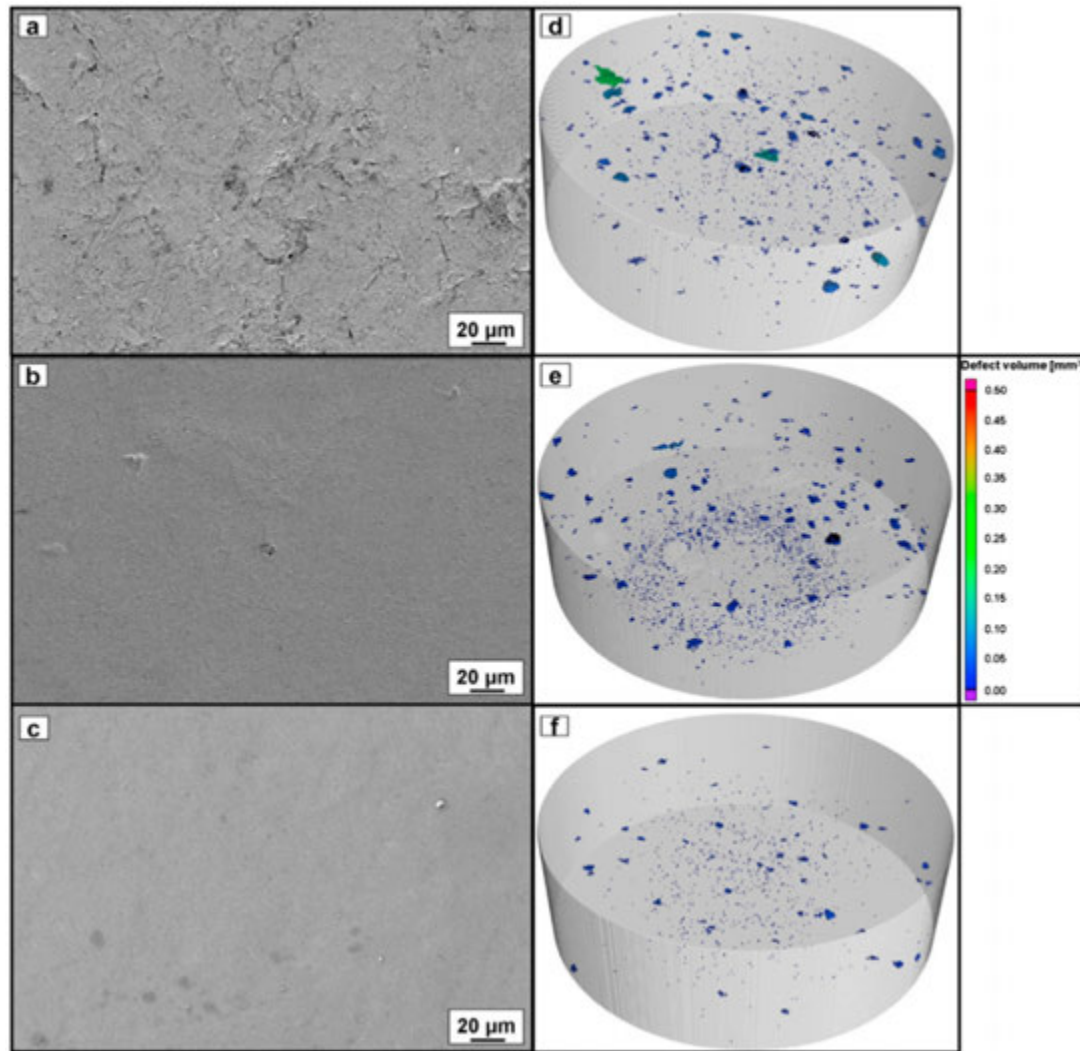


Fig. 7 (a–c) SEM images of Al-0.5CNT produced under 30, 50, 80 MPa, respectively, and (d–f) CT results of 3D porosities distributions. Reproduced from Singh, L.K., Bhadauria, A., Oraon, A., Laha, T., 2019. Spark plasma sintered Al-0.5 wt% MWCNT nanocomposite: Effect of sintering pressure on the densification behavior and multi-scale mechanical properties. *Diam. Relat. Mater.* 91, 144–155.

mechanisms of the nanocomposites. Surface diffusion, as the main grain coarsening mechanism with a lower activation energy, is more activated at lower temperatures. Thus, with higher heating rates, the materials spend less time at a lower temperature range leading to the limitation of the coarsening mechanisms. It should be mentioned that at lower heating rates the sintering mechanisms are inactive due to the available lower thermal energy. The density of the produced materials intensively is related to the sintering temperature. The relative density of the Al-SiO₂ nanocomposites was increased linearly until near full densification, as a function of the sintering temperature. In the case of the SPS process, plastic deformation, grain boundary, volume diffusion, and power law dislocation creep mechanisms are facilitated by increasing the sintering temperature. The hardness, yield strength, tensile strength, and elongation were increased by increasing of the sintering temperature as shown in Fig. 8(a). Also, with increasing the applied pressure from 30 MPa to 50 MPa, the density, hardness, yield strength, tensile strength, and elongation were increased as depicted in Fig. 8(b).

Ma *et al.* (2018) produced the Inconel 718 matrix composite reinforced by graphene oxide (GO) by the 3D milling and SPS process. The SPS process was carried out at a pressure of 30 MPa, holding time of 5 min, heating rate of 100°C min⁻¹, and various sintering temperatures of 850, 900, and 950°C. The effect of the sintering temperature on the microstructure and mechanical properties of the nanocomposites was investigated. By increasing of the sintering temperature, as an aggravation of diffusional reaction, the relative density increased and the porosity decreased. Moreover, the finest grain size was attained at the sintering temperature of 950°C, which is depicted in Fig. 9(a–c). The densification and consolidation were accelerated at higher sintering temperatures, as a result, the higher relative density and better mechanical properties were obtained. The micro-hardness, yield strength, and compressive strength of the nanocomposite which was sintered at 950°C, were 375 HV,

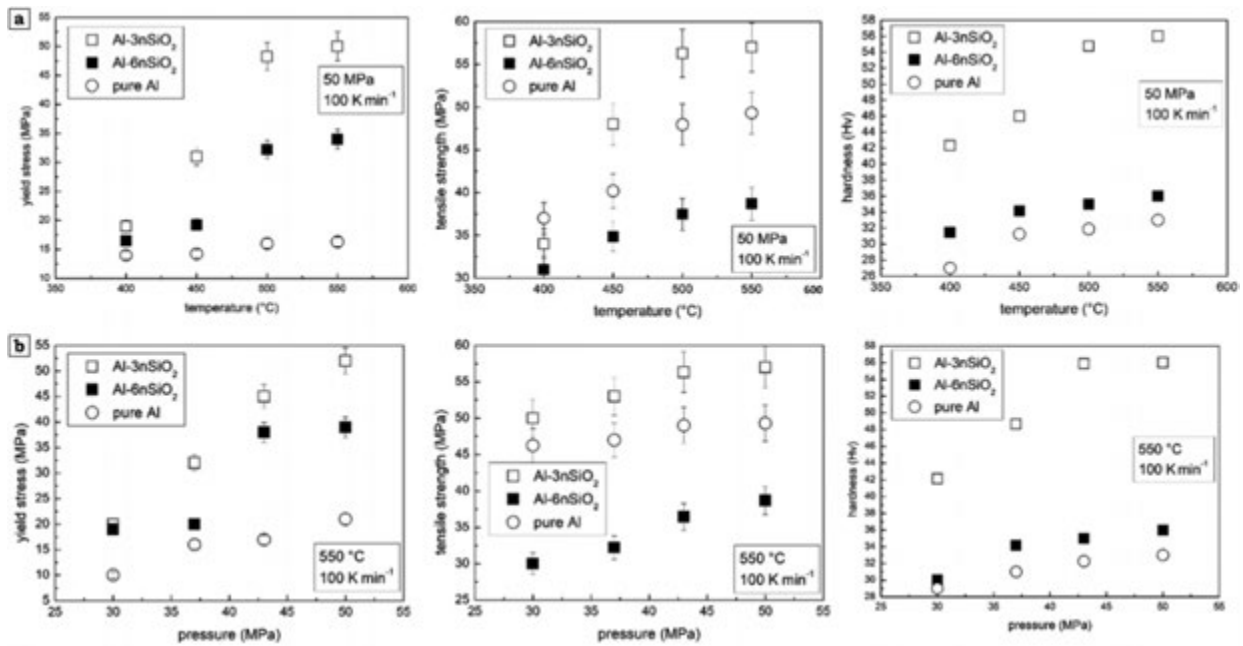


Fig. 8 Variation of the yield strength, tensile strength, and hardness of the pure Al, Al-3nSiO₂ and Al-6nSiO₂ nanocomposites as a function of pressure and temperature. Reproduced from Sadeghi, B., Shamanian, M., Ashrafizadeh, F., Cavaliere, P., 2018a. Effect of processing parameters on microstructural and mechanical properties of aluminum-SiO₂ nanocomposites produced by spark plasma sintering. *Int. J. Mater. Res.* 109, 422–430.

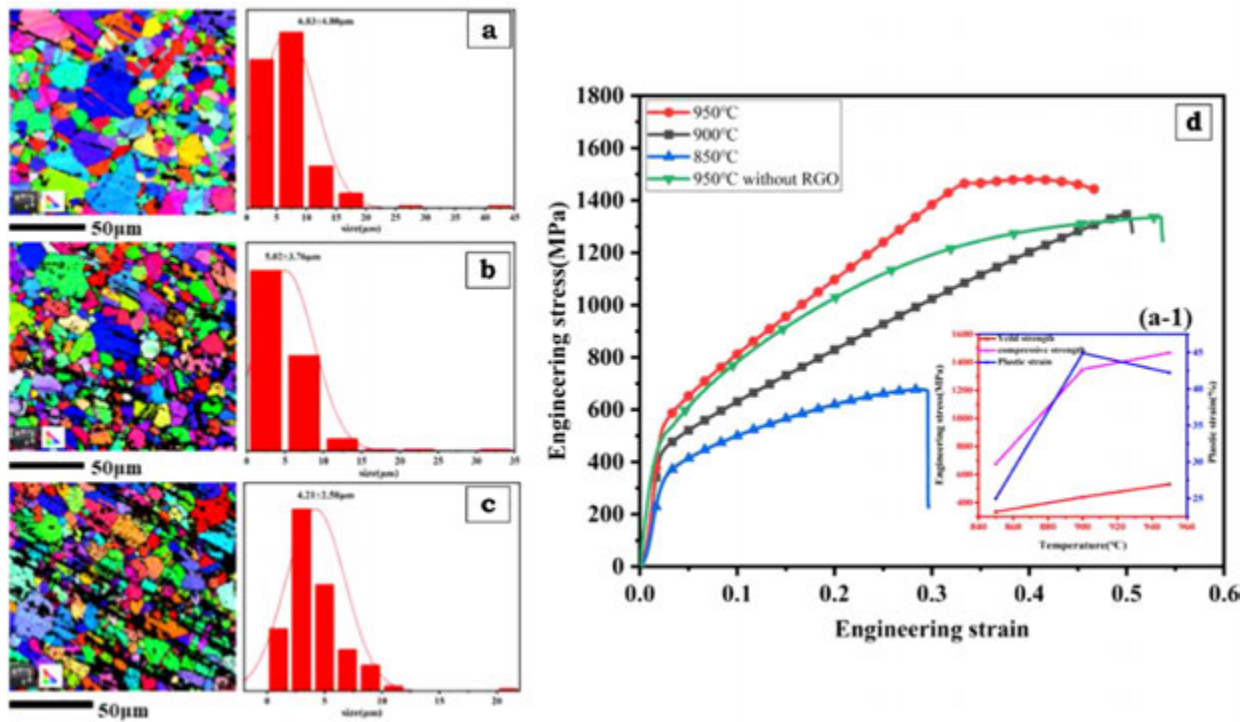


Fig. 9 Electron backscatter diffraction (EBSD) and grain size histogram of samples sintered at different temperatures (a) 850 °C, (b) 900 °C, (c) 950 °C, and (d) the stress–strain curve of the nanocomposites with different sintering temperatures. Reproduced from Ma, S., Yang, Y., Li, A., *et al.*, 2018. Effects of temperature on microstructure and mechanical properties of IN718 reinforced by reduced graphene oxide through spark plasma sintering. *J. Alloys Compd.* 767, 675–681.

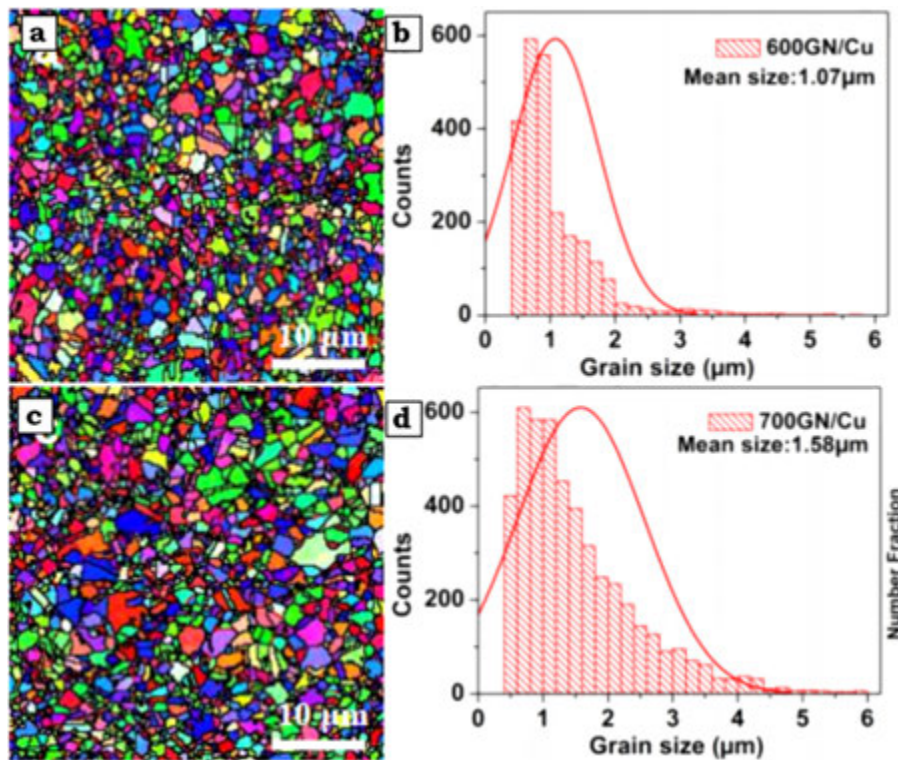


Fig. 10 EBSD analysis of the grain size distribution for different sintering temperatures: (a and b) 600°C, and (c and d) 700°C. Reproduced from Sun, C., Zhang, X., Zhao, N., He, C., 2019. Influence of spark plasma sintering temperature on the microstructure and strengthening mechanisms of discontinuous three-dimensional graphene-like network reinforced Cu matrix composites. *Mater. Sci. Eng. A* 756, 82–91.

530 MPa, and 1467 MPa, respectively. The stress–strain curves of the nanocomposites at different sintering temperatures are shown in Fig. 9(d).

Sun *et al.* (2019) demonstrated the production of the Cu/graphene nanocomposites using a 3D network and SPS process and also the effect of sintering temperature on the microstructure and mechanical properties was investigated. The SPS process conditions were selected to be as pressure: 50 MPa, holding time: 10 min, and sintering temperatures: 600, 650, and 700°C. The EBSD micrograph of the nanocomposite sintered at 600°C and 700°C is shown in Fig. 10. They had reported with increasing the sintering temperature, the defect on graphene and its interface with matrix was increased and also the mean grain size was increased from 1.07 μm to 1.58 μm, as illustrated in Fig. 10. Increasing of the sintering temperature accelerates the grain boundaries movement; thus, grains growth rate elevated. The tensile stress–strain curves, strain hardening rate, and Vickers hardness of the nanocomposite sintered at different temperatures are shown in Fig. 11. By increasing of the sintering temperature, the hardness, yield strength, ultimate strength, and also the ductility of the nanocomposites decreased. These reductions in mechanical properties could be attributed to the grain growth, defect increasing on graphene, and poor interfaces. A review of the sintered density, relative density, Vickers microhardness, young's modulus, tensile strength, elongation, and average grain size of metal matrix composites fabricated by the SPS process as a function of the composite composition and process parameters are illustrated in Table 1.

Ceramic Matrix Composites

The production of ceramic-based materials from ceramic powders with a fine microstructure was a big challenge due to the high sintering temperature and prolonged holding time in conventional sintering processes. Recently, these issues were solved by using of the SPS process, considering its lower sintering temperature and shorter holding time. Most of the ceramic-based composites were produced by the SPS process in recent years, among them, ultra-high temperature ceramics (UHTCs) with a melting point of higher than 2000°C, Al_2O_3 , and mullite are the most utilized materials. Based on the application of the ceramic composites, the reinforcement could be a whisker, particle or plate such as carbon fiber, oxides, carbides, nitrides, borides or most high-tech carbon-based nanomaterials like graphene and CNT.

Shen *et al.* (2002) reported the production of consolidated Al_2O_3 ceramic material at a much lower temperature (1150°C) in a short holding time (3 min) near full densification. The strong dependence of grain growth to the sintering temperature was suggested, which showed the nanostructure materials could be produced at a lower sintering temperature. Kumar *et al.* (2016) produced Al_2O_3 /10%TiC nanocomposites using of the MA and SPS process. The effect of the sintering temperature on the microstructure and mechanical properties was investigated. The SPS process was carried out at a heating rate of $50^\circ\text{C min}^{-1}$, pressure of 60 MPa, holding

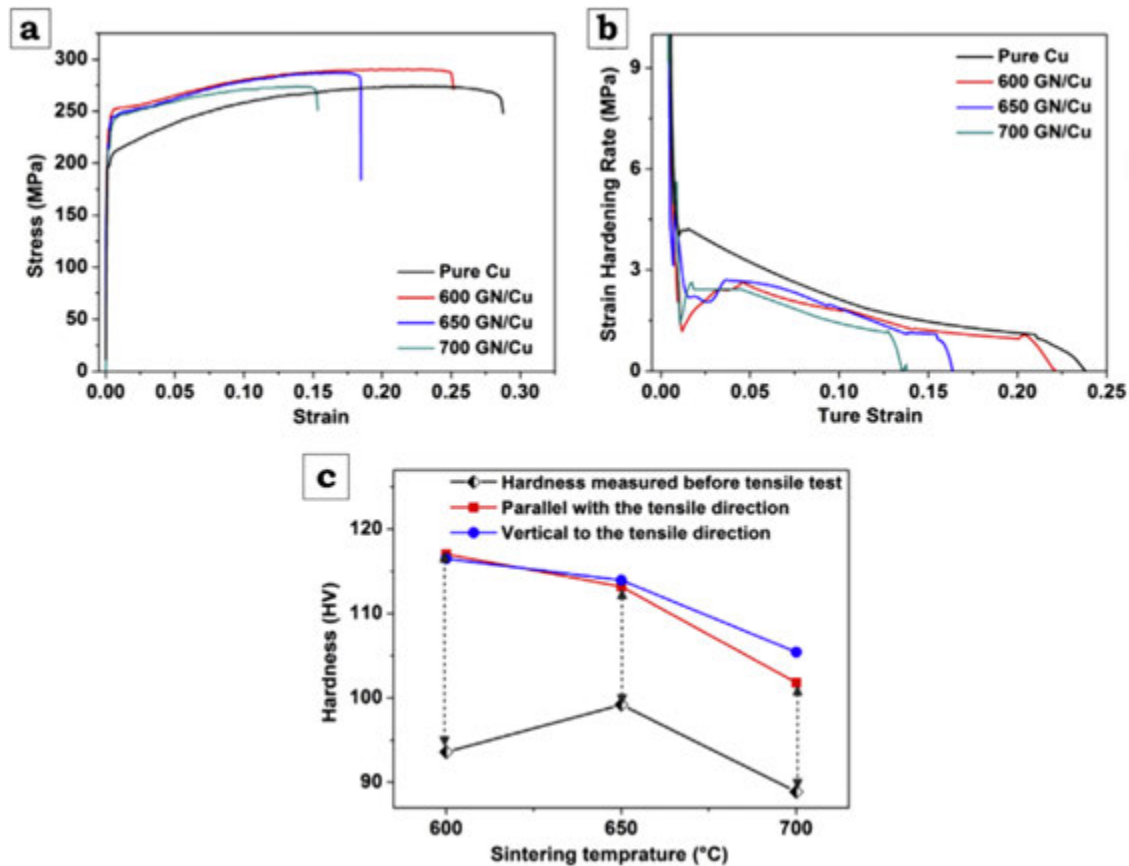


Fig. 11 Stress–strain curves, strain hardening, and hardness of the nanocomposite sintered at 600, 650, and 700°C. Reproduced from Sun, C., Zhang, X., Zhao, N., He, C., 2019. Influence of spark plasma sintering temperature on the microstructure and strengthening mechanisms of discontinuous three-dimensional graphene-like network reinforced Cu matrix composites. *Mater. Sci. Eng. A* 756, 82–91.

time of 3 min, and various sintering temperatures of 1100, 1200, 1400, and 1500°C. With increasing the sintering temperature from 1100°C to 1500°C, the relative density and hardness were improved from 93.6% to 99.7% and from 889 HV to 1892 HV, respectively. Nieto *et al.* (2015) have investigated the effect of SPS process parameters on the sintering behavior of the Al₂O₃/graphene nanoplates (GNPs) nanocomposites. Various SPS conditions were used to sinter the nanocomposites at heating rates of 100°C min⁻¹, pressures of 45 MPa and 90 MPa, holding times of 3–10 min, and temperatures of 1100, 1300, and 1500°C. With increasing the sintering temperature from 1100°C to 1500°C the relative density and grain size are increased which are illustrated in Fig. 12. For the same nanocomposite composition, the same behavior was seen with the applied pressure increasing, thus the relative density and grain size are increased. However, at higher sintering temperature with increasing the holding time from 3 to 10 min, the relative density decreased and grain size increased. The reason for the lower densification of the nanocomposite in a longer holding time is almost unclear; however, it could be attributed to the graphitization of the GNPs which could cause gaseous by-products and as a result, the porosities could be increased.

Petrus *et al.* (2017) investigated the sintering behavior of the SiC/B/graphene nanocomposites which were produced by the MA and SPS process. The heating rate, pressure, holding time, and temperature were 100°C min⁻¹, 50 MPa, 30 min, and 1800°C to 1900°C, respectively. The improvement of the relative density, microhardness, and fracture toughness as the result of sintering temperature increasing from 1800 to 1900°C was reported. In another work, Bódis *et al.*, 2017 investigated the sintering of the SiC/graphene at lower sintering temperatures and shorter holding time. The produced nanocomposite powders were SPSed at sintering temperatures ranging from 1700°C to 1850°C, heating rate of 100°C min⁻¹, pressure of 50 MPa, and holding time of 5 min. The relative density of the nanocomposites increased enormously with increasing the sintering temperature from 1700°C to 1850°C. This behavior is in contrast with previous reports (Nieto *et al.*, 2015), which could be due to the lower sintering temperature and shorter holding time of the SPS process. It is well to mention that this behavior is encouraged by increasing the weight percent of the graphene reinforcement, which could be attributed to the conductivity of the graphene accelerating the consolidation process of the nanocomposites. The more the nanocomposites get densified, the better the mechanical properties achieved. Thus, the hardness, Young's modulus, and fracture toughness of the nanocomposite were increased as a function of sintering temperature, too, as shown in Fig. 13. Table 2 reviews the relative density, Vickers microhardness, Young's modulus, fracture toughness, flexural strength, and average grain size of ceramic matrix composites fabricated by the SPS process as a function of composite composition and process parameters.

Table 1 Review of the sintered density, relative density, Vickers microhardness, Young's modulus, tensile strength, elongation, and average grain size of different metal matrix composites as a function of the process parameters

Composite systems	SPS conditions				Density (g cm^{-3})	Relative density (%)	Young's modulus (GPa)	Vickers Microhardness (GPa)	Tensile strength (MPa)	Elongation (%)	Average grain size (nm)	Ref.
	Heating rate ($^{\circ}\text{C/min}$)	Pressure (MPa)	Holding time (min)	SPS temperature ($^{\circ}\text{C}$)								
Al-CNT	40	50	20	480	2.642	—	—	—	207.5	21.4	—	(Kwon <i>et al.</i> , 2010)
Al-CNT	40	50	20	500	2.647	—	—	—	199.7	20.2	—	(Kwon <i>et al.</i> , 2010)
Al-CNT	40	50	20	560	2.655	—	—	—	200.1	19.8	—	(Kwon <i>et al.</i> , 2010)
Al-CNT	40	50	20	600	2.655	—	—	—	198.8	18.6	—	(Kwon <i>et al.</i> , 2010)
Al-CNT	100	35	5	400	—	93.5	—	0.8042	—	—	52	(Saheb, 2015)
Al-CNT	100	35	20	500	—	95.2	—	0.9336	—	—	84	(Saheb, 2015)
Al-Al ₂ O ₃	200	50	5	550	—	91.69	—	0.9239	—	—	27.24	(Saheb <i>et al.</i> , 2015)
Al-Al ₂ O ₃	200	50	20	550	—	91.69	—	0.8219	—	—	27.24	(Saheb <i>et al.</i> , 2015)
Steel-TiB ₂	200	50	5	550	6.15	—	176	0.218	590	—	—	(Sulima <i>et al.</i> , 2015)
Steel-TiB ₂	200	50	20	550	7.52	—	216	0.412	1180	—	—	(Sulima <i>et al.</i> , 2015)
Steel-TiB ₂	200	35	5	1000	7.35	—	215	0.226	1080	—	—	(Sulima <i>et al.</i> , 2015)
Steel-TiB ₂	200	35	30	1100	6.25	—	198	0.229	710	—	—	(Sulima <i>et al.</i> , 2015)
Al-TiN	50	50	10	500	—	96.5	—	—	900	—	34.5	(Li <i>et al.</i> , 2017)
Al-CNT	100	35	20	450	—	94	—	1.157	—	4.1	—	(Najimi and Shahverdi, 2017)
Al-CNT	100	35	20	550	—	97	—	1.196	—	4.9	—	(Najimi and Shahverdi, 2017)
Al-CNT	20	30	60	527	—	—	—	—	186	—	175	(Chen <i>et al.</i> , 2017)
Al-CNT	20	30	60	627	—	—	—	—	210	—	172	(Chen <i>et al.</i> , 2017)
Ti-Al-V-TiN	100	50	30	1100	—	97.98	—	5.208	—	—	—	(Falodun <i>et al.</i> , 2018)
Ti-Al-V-TiN	100	50	30	1100	—	98.89	—	5.904	—	—	—	(Falodun <i>et al.</i> , 2018)
Ti-TiB ₂	50	50	5	750	4.17	—	—	2.089	397	3.74	—	(Mohammadzadeh <i>et al.</i> , 2018)
Ti-TiB ₂	50	50	5	1050	4.40	—	—	4.678	519	6.65	—	(Mohammadzadeh <i>et al.</i> , 2018)
Ti-TiB ₂	50	50	5	1350	4.41	—	—	5.306	539	5.9	—	(Mohammadzadeh <i>et al.</i> , 2018)
Ti-TiB ₂	50	50	5	900	4.372	98.46	—	—	490	3.82	—	(Mohammadzadeh <i>et al.</i> , 2020)
Ti-TiB ₂	50	50	5	1200	4.435	99.88	—	—	541	6.62	—	(Mohammadzadeh <i>et al.</i> , 2020)
Al-4Cu-graphene	50	50	10	500	2.82	99.26	—	1.226	320	10	—	(Khoshghadam-Pireyousefan <i>et al.</i> , 2020)

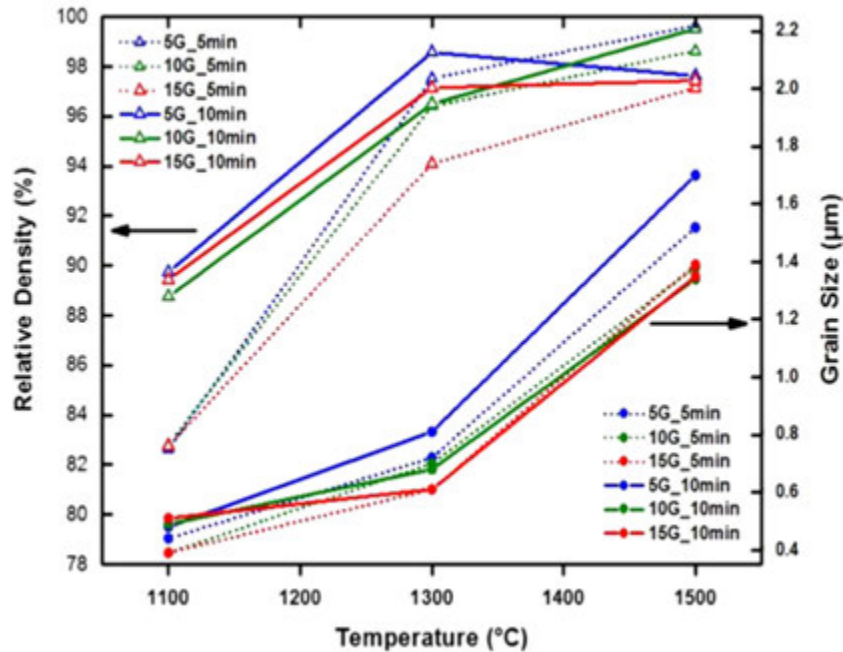


Fig. 12 The relative density and grain size of Al_2O_3 /graphene nanocomposites as a function of sintering temperature. Reproduced from Nieto, A., Huang, L., Han, Y.-H., Schoenung, J.M., 2015. Sintering behavior of spark plasma sintered alumina with graphene nanoplatelet reinforcement. *Ceram. Int.* 41, 5926–5936.

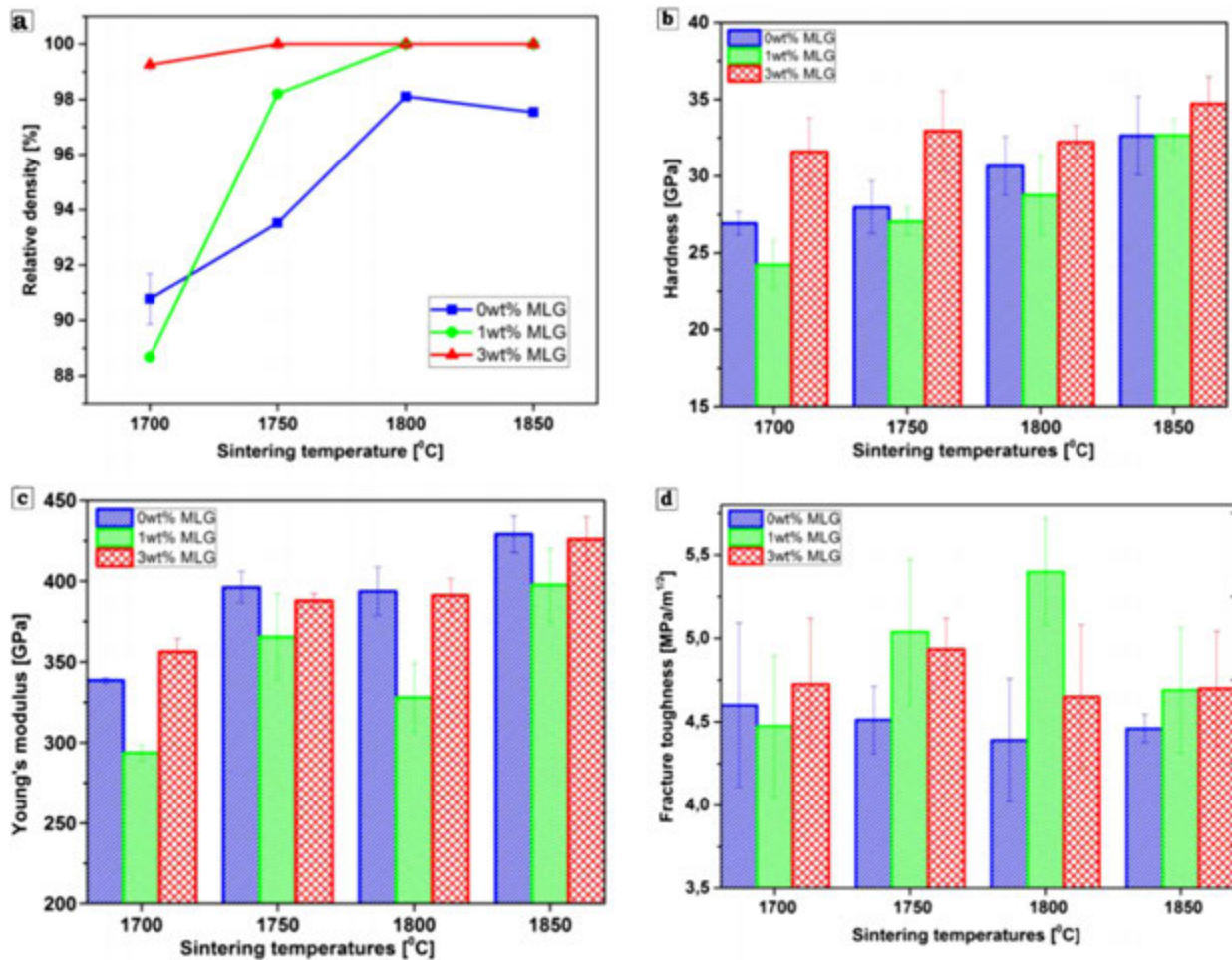


Fig. 13 (a) Relative density, (b) Vickers hardness, (c) Young's modulus, and fracture toughness of the SiC/graphene nanocomposites as a function of sintering temperature. Reproduced from Bódis, E., Cora, I., Balázi, C., *et al.*, 2017. Spark plasma sintering of graphene reinforced silicon carbide ceramics. *Ceram. Int.* 43, 9005–9011.

Table 2 Review of the relative density, Vickers microhardness, Young's modulus, fracture toughness, flexural strength, and average grain size of different ceramic matrix composites as a function of composites composition and processing parameters.

Composite systems	SPS conditions				Relative density (%)	Vickers microhardness (GPa)	Young's modulus (GPa)	Fracture toughness (MPa m ^{1/2})	Flexural strength (MPa)	Average grain size (μm)	Ref.
	Heating rate (°C/min)	Pressure (MPa)	Holding time (min)	SPS temperature (°C)							
HfB ₂ -SiC	100	30	23	2100	100	26	512	3.9	—	2	(Bellosi <i>et al.</i> , 2006)
ZrB ₂ -MoSi ₂	100	30	24	1750	97.7	16.2	479	4.4	—	1.4	(Bellosi <i>et al.</i> , 2006)
ZrB ₂ -ZrC-SiC	100	30	23	2100	99	18.8	474	3.5	—	2	(Bellosi <i>et al.</i> , 2006)
ZrB ₂ -SiC	17	30	4	1900	—	—	—	—	732	—	(Guo <i>et al.</i> , 2010)
ZrB ₂ -SiC-Yb ₂ O ₃	17	30	4	1900	—	—	—	—	426	—	(Guo <i>et al.</i> , 2010)
ZrB ₂ -SiC	100	30	4	1900	—	—	—	—	691	—	(Guo <i>et al.</i> , 2010)
ZrB ₂ -SiC-Yb ₂ O ₃	100	30	4	1900	—	—	—	—	670	—	(Guo <i>et al.</i> , 2010)
TaC-long CNT	200	255	10	1850	94	14.2	288	1.58	—	1.06	(Bakshi <i>et al.</i> , 2011)
TaC-short CNT	200	363	10	1850	104	10.6	258	1.08	—	1.65	(Bakshi <i>et al.</i> , 2011)
TaC-SiC	100	40	5	1600	98.6	19.2	511	4.9	599	—	(Liu <i>et al.</i> , 2012)
TaC-SiC	100	40	5	1700	99.1	19.6	512	6.1	611	—	(Liu <i>et al.</i> , 2012)
TaC-SiC	100	40	5	1800	99.3	19.9	517	6.4	682	—	(Liu <i>et al.</i> , 2012)
TaC-SiC	100	40	5	1900	100	20.3	537	6.7	715	—	(Liu <i>et al.</i> , 2012)
B ₄ C-CNT	150	40	—	1620	96.58	32.76	—	5.90	—	—	(Yavas <i>et al.</i> , 2015)
TiB ₂ -TaC	50	20	5	2000	> 98	28.8	—	5.9	—	2–4	(Demirskyi and Sakka, 2015)
Al ₂ O ₃ -TiC	50	60	3	1100	93.6	8.717	239	—	—	—	(Kumar <i>et al.</i> , 2016)
Al ₂ O ₃ -TiC	50	60	3	1200	95.6	10.88	338	—	—	—	(Kumar <i>et al.</i> , 2016)
Al ₂ O ₃ -TiC	50	60	3	1400	97.4	14.04	420	—	—	—	(Kumar <i>et al.</i> , 2016)
Al ₂ O ₃ -TiC	50	60	3	1500	99.7	18.55	628	—	—	—	(Kumar <i>et al.</i> , 2016)
Al ₂ O ₃ -TiC	40	40	7	1800	85.91	11.3	—	—	289	—	(Fattahi <i>et al.</i> , 2020)
Al ₂ O ₃ -TiC	40	40	7	1900	98.7	24.4	—	—	551	—	(Fattahi <i>et al.</i> , 2020)

Polymer Matrix Composites

The consolidation of polymer-based materials with the SPS process did not receive as interest and attention as metallic or ceramic based materials. Especially, in the case of polymer matrix composites limited researches have been reported. The most limited research works are available on Polyimide (PI). The production of the polymer/metal composites with the help of SPS process known as FGMs was developed by [Omori \(1994\)](#) and so the PI/Al FGM was produced via powder metallurgy route. Thanks to the die design, the temperature gradient along the PI and Al was good and despite the 85°C difference in the consolidation temperature of the PI and Al, this composite was manufactured in a one-step process. After the sintering process, cracks were found on PI, which was ascribed to the difference in thermal expansion of PI and Al leading to the relaxation of residual stresses. To solve this issue, the production of the FGM with several layers of PI/Al was suggested. In other research, they replaced Al with Cu to produce PI/Cu FGM ([Omori et al., 1997](#)). Three layers of Cu and PI powders were used and densified FGM without any cracks was produced. [Tanaka et al. \(2004\)](#) were developed the PI matrix composites reinforced by carbon and diamond for wear and friction applications with the help of the SPS process. The mixed powders were consolidated at a sintering temperature of 220°C and pressure of 50 MPa. Also, some composite samples sintered at 250°C and 280°C; however, some cracks were found on samples and the anti-wear properties of the composites were degraded.

[Wei and Nolas \(2018\)](#) were investigated the thermoelectric properties of poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/inorganic nanoparticle composite which was produced by the SPS and HP process. The SPS process temperature, pressure, holding time, and heating rate were 100°C, 60 MPa, 30 min, and 10°C min⁻¹, respectively. As compared to the HPed EG doped PEDOT: PSS, the ZT value improvement of 0.04 at 45°C was achieved with two orders of magnitude for composites with 20 wt% Bi_{0.5}Sb_{1.5}Te₃ and 20 wt% EG doping in PEDOT: PSS consolidated by SPS. The better properties of SPS consolidated samples is due to the lower damages caused by the SPS process on polymer chains leading to the better conductance of the samples.

[Adesina et al. \(2019\)](#) have reported the fabrication of the graphene reinforced polylactic acid nanocomposite by the SPS process, in which, the SPS process parameters were optimized using the response surface method and analysis of variance. The SPS process was carried out at the heating rate of 20°C min⁻¹, holding time of 10 min as constant parameters and pressure of 17–32 MPa and temperature of 120°C–160°C as variable parameters. The results showed that the density and hardness of the nanocomposites are related to both sintering pressure and temperature and improved as a function of pressure and temperature. The most desirable density (1.28 g cm⁻³) and Vickers hardness (260 HV) of the nanocomposites obtained in sintering pressure and temperature of 25.87 MPa and 158.2°C, respectively, which was reported as optimum condition.

Conclusion

The SPS process as a new generation of consolidation and sintering process has attained significant attention not only by academic researchers but also in industrial-scale applications. Despite the SPS process only being in its third decades of development, the individual characteristics of the process in industries such as aerospace, automotive, and electronic have been distinguished and compared to the other traditional sintering processes. Due to the lower duration of the consolidation process, it is known as a time and energy cost-effective process. Many types of materials such as composites, nanocomposites, and magnetic materials have been and are being produced by the SPS process, which were traditionally produced by other techniques. However, in the case of the SPS process, the better properties such as higher strength, higher hardness, higher wear resistance, and higher conductivity have been achieved. The physical property advantages of the SPS process compared to the other sintering methods could be attributed to the higher heating rates, shorter holding times, and higher cooling rates which lead to greater consolidation efficiency. With regard to these advantages, the microstructure is also controllable during the SPS process and fine grained and nanostructured materials can be easily produced.

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Materials Used Within Polymer Matrix Composites (PMCs) and PCM Production Via Additive Manufacturing

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Glossary

Additive manufacturing Is a class of technologies that builds parts layer by layer using digital 3D design data.

Aspect ratio The ratio of length to width of a particle.

CNTs Carbon Nanotube.

Composite A complex material with two main parts: the matrix and the reinforcing phase.

Nanoparticle Are particles between 1 and 100 nanometers (nm) in dimension.

Introduction

In the past years, the best material types for components of high rigidity, strength, resistance to heat and chemical products, and availability, have been metals and ceramics. These materials provided an appropriate set of properties for the manufacture of parts used in industries such as aerospace, automotive, and medicine. With the introduction of new polymer nano-reinforced composites, novel replacement options for traditional materials are now available to the design engineer. The composite consists of two main parts: the matrix and the reinforcing phase. The matrix surrounds the reinforcement materials, holding it in its relative position. Via a combination of the reinforcement and matrix properties, the reinforcement materials improve the composite material mechanical properties (Feldman, 2013).

Composites can be classified in terms of biological: (1) Natural composites such as bone, muscle, and wood, and (2) synthetic composites (engineered). This second classification of composites are in terms of matrix phases: ceramic-based composites (CMC), polymer-based composites (PMC), and metal-based composites (MMC). Metals or polymers are commonly used as a matrix material. In ceramic composites, the reinforcement is chosen to improve the fracture toughness. A most important factor in choosing the matrix and reinforcement is the resultant bond strength and combined physical properties (Matthews and Rawlings, 1999).

Ceramic-based composites (CMCs): Due to resistance to high temperature oxidation, despite the possibility of brittle failure, this classification is used for high temperature and severe stress applications. Compared with ceramics and other materials, ceramics can be readily used at high temperatures and provide high hardness and strength. They also have low density, thermal expansion coefficient, and low electrical and thermal conductivity. Particularly, the density and low thermal expansion of ceramics are of great importance in most applications. The ratio of the modulus of elasticity between the reinforcement and the metallic or polymeric matrix in composites is generally between 10 and 100. For ceramic matrix composites, this ratio is usually one or less (Bhaduri and Froes, 1991).

Metal-based composites (MMC), compared to polymeric matrix composites, provide higher performance temperature, non-flammability and greater resistance to the invasion of organic fluids. However, they are generally more expensive. Super alloys, iron, aluminum, magnesium, titanium, and copper based alloys are used as matrix materials. Reinforcing materials may be in the form of particles, continuous filaments, discontinuous filaments, or whiskers that make up 10%–60% by volume of the composite. Carbon, silicon carbide, tungsten carbide, boron, alumina, and refractory metals are common reinforcement materials. (Clyne and Withers, 1995).

Polymeric matrix composites consist of a polymeric resin as a matrix with a reinforcing agent. The characteristics of these composites include their wide range of applications, good properties at ambient temperature, ease of manufacture and low cost. These types of composites are divided into glass, carbon, and aramid. Glass fiber polymer composite consists of continuous or discontinuous glass fiber filaments in the polymer. Carbon fiber reinforcing filament use as reinforcing phase is expected to increase in usage relative to glass fiber filament usage, since the carbon fibers have the highest specific strength and specific modulus among the reinforcement materials. Aramid fibers, introduced in the early 1970s, offer an alternative reinforcing phase also providing high strength and modulus (Piggott and Harris, 1980).

The interest in nanocomposites worldwide has led many research centers to study the potential applications of these materials. The first successful attempts at nanocomposite development date back to the sixties. However, the Japanese company Toyota that made nylon 6 and clay based nanocomposites in 1980. Since then, other companies have studied nanocomposites for other commercial applications, and in late 2001, General Motors and Basell released the first nanocomposites based on thermoplastic olefins for use in automotive exterior components (Walter *et al.*, 1999).

The increasing need for fuel efficiency has increased the demand for new lightweight materials such as polymer composites. The relatively high cost and heavy weight of metal and glass materials have therefore spurred interest materials with lower density. Another important advantage of polymeric materials is their ease of formability (Young and Lovell, 2011).

However, the use of polymer materials without reinforcement has been limited, due to their relative weakness in mechanical, chemical and thermal properties. The use of nanoparticles and nanofillers into the polymer matrix can overcome these deficiencies. Polymer nanocomposites (PNC) include a polymer or copolymer which are reinforced with a homogeneous distribution in the matrix of nanometer scale particles or fillers. These are fabricated by a variety of methods such as physical blending or chemical polymerizing technologies. For polymeric nanocomposites, at least one of the dimensions of the filler or particles is at the nanoscale, resulting in improved final products' properties such as mechanical, chemical or thermal properties (Christopher and Celestine, 2012).

Considerable research and development has resulted in options where only relatively low volumes of reinforcement have been required resulting in the increased use of polymeric nanocomposites. Polymer nanocomposites have been considered in engineering applications such as automotive, aerospace, building and medical equipment (Amanat *et al.*, 2010).

Nanocomposites are the preferred materials for use in engineering applications in advanced industries, due to the extraordinary properties they can possess, such as high stiffness, high strength, and low weight. These properties are due to the embedded nanoparticles reinforced phase into the polymer matrix [10–13]. Reinforcing polymers with common materials damages the two main characteristics of polymers, the lightness, and ease of processability. Hence, in recent research, low amounts (less than 10% by weight) of nanoparticles are typically used for polymer reinforcement (Hassanzadeh-Aghdam *et al.*, 2017).

Structure

Nylon 6 was the first polymer used by Toyota in 1990 to make nanocomposites, whereas today thermoset polymers such as epoxy, polyimide and thermoplastic polymers such as polypropylene, polystyrene are used as the matrix material of this composite (Mathias *et al.*, 1999). In developing multicomponent materials, whether nanoscale or micro-scale, three independent subjects have to be considered: component selection, production, processing and efficiency. In the case of polymer nanocomposites, we are still at the early stages of development of this material genre, and given the demand from the end applications, there are many areas for development.

In the methods of producing polymer nanocomposites and distinguishing them from each other, a homogenous dispersion of reinforcement material and bonding with the polymer matrix are most important. Surface modification can help make the distribution uniform by preventing agglomeration of the nanometric filler material and also enable chemical bonding with the matrix (Rong *et al.*, 2006).

One of the most recent and widely used production methods which has attracted the attention of many researchers is additive manufacturing. Additive manufacturing is becoming an efficient way to build complex structures with high precision and good performance. Thermoplastic, thermoset or even elastomer (rubber) polymers can be used in the 3D printing process. 3D printing offers several advantages in the production of composites including high precision and custom geometry. Therefore, the use of this technique in the medical, jewelry, automotive, aerospace, electronics and apparel industries has already been considerable (Wong and Hernandez, 2012).

Fabrication techniques of composites create products with complex geometry through material removal processes. While the manufacturing process and performance of composites in these methods are well-controlled and understood, the ability to control the complex internal structure is limited. The development of these nanocomposites, with the help of Additive Manufacturing Technology, is a challenge. Compared to traditional manufacturing technologies, AM offers many exclusive advantages in terms of material efficiency, straightforward operation, and greater design flexibility.

There are different methods to produce polymer nanocomposites by additive manufacturing which depends on the type of materials and final product applications. The most important methods are Stereolithography (SLA), Fused deposition modeling (FDM), Selective laser sintering (SLS), and Ink-jet Printing. Common polymers which are used in this technology include Polylactic acid (PLA), Acrylonitrile butadiene styrene (ABS), Polyvinyl alcohol (PVA), Polycarbonate (PC), Nylon, and Polyethylene terephthalate (PET) (Ligon *et al.*, 2017).

Nanomaterials

Nanotechnology is the know-how of how tools and systems can be operated to produce nanometer scale, or atomic and molecular level, material structure control.

By changing the dimension of materials from the micro-scale to the nanoscale, a significant change in some of the physical and chemical properties can be seen. The most important are: increasing the surface area to volume ratio and changing the particle size into the realm of quantum effects. An increase in the surface area to volume ratio, which occurs gradually with decreasing particle size, changes the behavior of the atoms located at the surface of the particle toward that of the behavior of the inner atoms. This phenomenon affects the properties of the particle and its interactions with other substances (Edelstein *et al.*, 1997).

Since these particles are small enough, they begin to exhibit quantum behavior. The properties of quantum dots are an example of this. Quantum dots are nano-sized crystals that emit light and are widely used in medical diagnosis. These are sometimes called synthetic atoms, because their free electrons occupy discrete and virtual states of energy similar to the electrons trapped in atoms (Biener *et al.*, 2009).

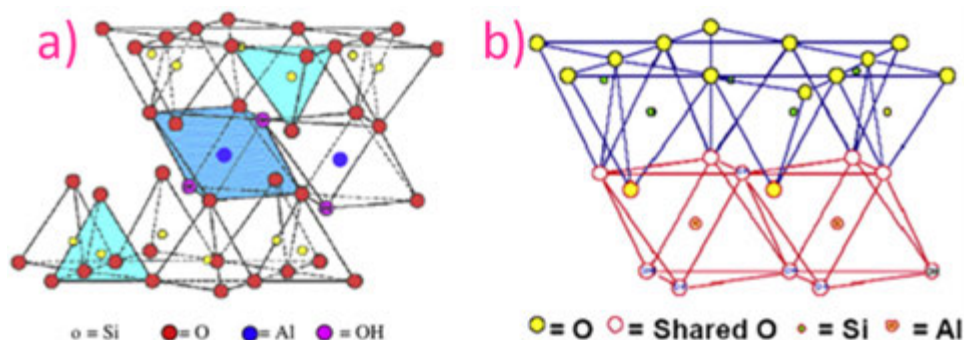


Fig. 1 (a) Structure of montmorillonite (MMT) clay, and (b) structure of kaolinite clay. Reproduced from Barua, S., Gogoi, S., Khan, R., Karak, N., 2019. Chapter 8 – Silicon-based nanomaterials and their polymer nanocomposites. In: Karak, N. (Ed.), *Nanomaterials and Polymer Nanocomposites*. Elsevier, pp. 261–305.

Dimensional Classification of Nanomaterials

A common categorization in nanomaterials is the division of nanomaterials by the number of dimensions in the nanometer range. If all external dimensions of a material are in the nanoscale, it is called the zero-dimensional (0D) that is, between 1 and 100 nm such as nanoparticles (fullerene), quantum dots (such as CdSe, CdS, etc.) and nanoclusters. Likewise, if two external dimensions of the material are in the nanoscale range, the third one being usually at the microscale, that is one-dimensional (1D) nanostructures (Nano rod, Nanowire and Nanotube). Two-dimensional nanomaterials (2D) have one dimension in the nanoscale (thin films, Nanoplate and Nanosheet) (Dolez, 2015).

Polymer Matrix Nano-Ceramic Reinforced Composites

The advent of nanoceramic reinforcements can be traced back to the 1990s. At this time, due to the very desirable properties of nanoceramic powders, attention was drawn to them, but their processing methods were not easy and affordable. Nanoceramics are ceramics whose primary components are in the nanoscale (such as nanoparticles, nanotubes, and nanolayers). They possess properties such as good heat resistance, optical and electrical properties, superconductivity at higher temperatures, the ability to transmit light, and compatibility to the body (Barsoum and Barsoum, 2002).

The most important raw materials for ceramics are material oxides, clay, feldspar, silica (quartz sand) and limestone. Special ceramics, such as electric ceramics, use talc, sodium compounds, titanium, and metallic elements. Clay forms the majority of ceramics such as Kaolinite. Ceramics, in terms of their use, are divided into traditional ceramics such as tile pottery, are made from minerals such as clay and silicate, and the other one is modern ceramics (engineering) which are classified to oxide ceramics such as beryllium oxide (BeO), titanium oxide (TiO₂), aluminum oxide (Al₂O₃), zirconium oxide (ZrO₂), etc. and non-oxide ceramics such as silicon nitride (Si₃N₄), boron nitride (BN), silicon carbide (SiC), and titanium carbide (Worrall, 1986).

Due to the weaknesses of the polymers in their strength and hardness and their low temperature tolerance, nanoceramics are added to polymers. Full dispersion of the nanoclays into the polymer matrix is usually difficult or impossible, therefore, to achieve this goal, the nanoclay surface is treated or the coupling agent or compatibilizer are used. For instance, Kasiri *et al.* used organophilic montmorillonite (OMMT) nanoclay to improve the thermal properties of polyethylene nanocomposite, which utilized polyethylene graft maleic anhydride (PE-g-MA) as a compatibilizer for better dispersion of nanoclay in the polymer matrix which resulted to improved thermal conductivity and burning rate properties (Kasiri *et al.*, 2015). MMT is referred to as a member of the smectite group with 2:1 silica-alumina ratio. (Fig. 1(a)). The researchers found that the high aspect ratio of MMT clay plays a key role in the reinforcement of this nanoclay in polymer nanocomposites. MMT clay is swollen and expands due to its hydrophobic properties when exposed to water. Therefore, pristine MMT is highly compatible with hydrophilic polymers such as Poly (vinyl alcohol), Poly (vinyl acetate), Poly(ethylene glycol), etc. It is also used as a component of drilling mud in oilfield drilling applications to cool drill bits. Another of the most widely used clay is the kaolinite which the first time its structure introduced by Pauling which is formed by 1:1 ratio of tetrahedral silica and octahedral alumina units. Kaolinite is made up of 46.54% of silica, 39.50% of alumina, and 13.96% of water with a net negative charge (Fig. 1(b)). Many researchers have used modified Kaolinite (to overcome agglomeration in a polymer matrix) to reinforce polymer nanocomposites that are widely used in various industries. The results showed that kaolinite improved toughness, impact strength, and thermal stability in the nanocomposite. kaolin also indicates the most significant enhancement in melt flow index (MFI) and degree of crystallization (DOC) beyond other composites (Ariffin *et al.*, 2008). Additive manufacturing technology (stereolithography method) has been used to produce nanoclay-reinforced polymer nanocomposites (Eng *et al.*, 2017). In this study, the researchers used plate-shaped montmorillonite as well as a photo-polymer. The results showed that mechanical properties such as elongation, Young's modulus and tensile stress were significantly improved.

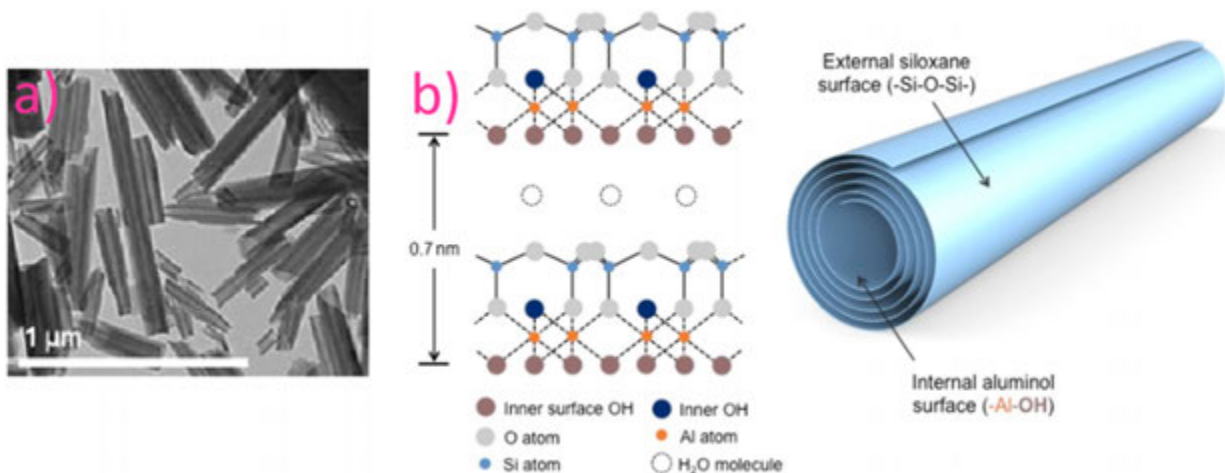


Fig. 2 (a) Morphology of Halloysite (b) structure of Halloysite. Reproduced from (a) Vinokurov, V.A., Stavitskaya, A.V., Chudakov, Y.A. *et al.*, 2017. Formation of metal clusters in halloysite clay nanotubes. *Science and Technology of Advanced Materials* 18 (1), 147–151. doi:10.1080/14686996.2016.1278352. (b) de Oliveira, A.D., Beatrice, C.A.G., 2018. Polymer nanocomposites with different types of nanofiller. In: Sivasankaran, S. (Ed.), *Nanocomposites-Recent Evolutions*. IntechOpen.

Another most commonly used nano clay is multiwalled aluminosilicate, known as halloysite, which is a natural mineral resource with great capability for use in a variety of industrial applications. Halloysite is chemically similar to kaolinite and has unique properties such as high strength, easy dispersion into the matrix of various conductive and insulating polymers and more importantly its abundance and environmental compatibility (Nazir *et al.*, 2016). Halloysite nanotubes are formed by rolling aluminosilicate sheets, these nanotubes have same mechanical properties like carbon nanotubes. Research has shown that these natural nanotubes are composed of silicon and aluminum and hydrogen which provide the required properties for various electrical and medical applications (Kamble *et al.*, 2016). The structure and morphology of halloysite are shown in Fig. 2. Guo *et al.*, for example, used the super hydrophobic property of halloysite to produce a superabsorbent for oil – water separation (Guo *et al.*, 2018). Kamalieva also used halloysite due to its compatibility with the body in medical applications (Kamalieva *et al.*, 2018). Wu *et al.*, by adding halloysite nanotubes (HNTs) as coatings on polylactic acid (PLA) were able to produce polymer nanocomposite by additive manufacturing technology in which 3D printed PLA with HNTs coatings improved adhesion and cell proliferation (Wu *et al.*, 2019).

Barium titanate has excellent dielectric, ferro and piezoelectric properties. It is considered one of the most important types of nanoceramic materials. Barium titanate is a high-energy dielectric coefficient material that has wide applications in the manufacture of electronic components such as multilayer capacitors for electrical resistors, piezoelectric sensors as well as electrical and optical devices (Reynolds *et al.*, 2012).

Hydroxyapatite (HA) is one of the most important bioactive ceramics that has wide clinical applications in dentistry, orthopedics and biomaterials because of its biocompatibility and structural similarity to the mineral part of bones and teeth (Suchanek and Yoshimura, 1998; Swetha *et al.*, 2010). Bioactive ceramics are used as coatings on high-strength and high-performance packages, such as implants, to repair bones, joints and teeth during injury, as well as pyrolytic carbon coatings. They are also used in heart valves and special radioactive glasses for the treatment of specific tumors and as coatings on metal substrates (Vyavahare *et al.*, 1997).

Today, calcium phosphates and calcium sulfates are good examples of absorbable ceramics in to polymer nanocomposites. To date, most of the work on ceramic implantation in animal body and clinical applications has focused on tricalcium phosphate and hydroxyapatite. Tricalcium phosphates are generally considered biodegradable, although some differences have been reported depending on the material used (Miao *et al.*, 2008).

Many researchers today use silica nanoparticles to reinforce polymer composites. One of the most widely used polymers in the industry is epoxy resin. Epoxy has properties such as high strength, low shrinkage after molding, high adhesion to many surfaces, high electrical and chemical resistance (Boyle *et al.*, 2001).

Silica has high hardness, strength, and high melting point, and although a relatively neutral element, it reacts with halogens and alkalis and most acids have no effect on it except a combination of nitric acid and hydrofluoric acid. Jun and Liang, in their research, improved the mechanical properties of epoxy resin by adding nanosilica to the polymer matrix. Their results showed that adding a small amount of nanosilica to the epoxy resin would increase the strength and toughness of the epoxy, while adding more nanosilica to the polymer matrix would reduce the strength and toughness (Ma *et al.*, 2008; Liang and Pearson, 2009). Tjong showed that adding only 5% by weight of nano-silica to PA6 significantly improved its mechanical properties (Tjong, 2006). Zhou *et al.* are among those who have conducted extensive research on the effect of colloidal silica and nano-silica on acrylic and polyester-based polyurethane composites and found that the addition of both hydrophobic and hydrophilic nano-silica improved the physical and mechanical properties such as scratch and abrasion resistance (Zhou *et al.*, 2004; Chen *et al.*, 2005).



Fig. 3 The fullerene atomic structure of a zero-dimensional nanostructure made of carbon atoms. Reproduced from Yadav, B.C., Kumar, R., 2008. Structure, properties and applications of fullerenes. *International Journal of Nanotechnology and Applications* 0973 (1), 15–24.

Polymer Matrix Nano-Carbon Reinforced Composites

As mentioned before, different additives are used to reinforce polymer composites. One of these essential and widely used additives are nano-carbons to improved polymer composite properties. There are several types of nano carbons which the most important are carbon nanotubes, fullerenes, carbon diamond, carbon graphite, graphene, etc. (Nasir *et al.*, 2018).

Fullerenes

Fullerene is an allotrope of carbon such as diamond, graphite and carbon nanotubes and has a structure like graphite, but in addition to hexagonal structures, there are pentagons of carbon atoms. Fig. 3 shows the fullerene structure. This zero-dimensional nanostructure has 20 hexagons and 12 pentagons (Pierson, 2012).

Fullerene has been of great interest to researchers because of its unique structure and optical, mechanical, biocompatibility, drug delivery, and numerous other properties. To this end, much research has been done on the functionalization and bonding of fullerenes to different polymers and molecules to increase their solubility and improve their properties and has led to the development of new nanocomposites in various fields (Chen *et al.*, 1998).

Fullerenes were also used as an agent for flame retardancy, for instance, Index Oxygen Limiting from 22.5 for pure epoxy to 30 for the epoxy-/(O-C60-(BEN CL88)-O-C60-(BEN Clay)) composite (Tsai *et al.*, 2015). Moreover, Addition of fluorine to the polymer matrix also improved the mechanical properties of composites such as increased strength and hardness (Okonkwo *et al.*, 2015).

Fullerenes are suitable acceptors for electrons in solar cells, especially organic and polymer solar cells, due to the rapid transfer of electrons from fullerene-bound polymers to the fullerene structure. For example, polymers such as P3HT poly (3-hexylthiophene) acting as donor and PCBM ([6,6] -phenyl-C61-butyric acid methyl ester) acting as electron acceptor can be attached to fullerenes and, as a result, their solubility improves substantially, and even functionalized fullerenes with groups such as cyanobiphenyl can be used. However, the use of these systems has not yet reached commercialization for two reasons: their band gap is large, thus they can absorb a small percentage of the solar spectrum. also due to phase discontinuities, transfer and collection of electrostatic are delayed (Zhu *et al.*, 2009; Wang *et al.*, 2012).

Carbon nanotube

Carbon nanotubes are divided into single-walled and multi-walled nanotubes, which single-walled nanotubes are divided into three major categories, armchair and chiral which indicate the metal properties, and Zigzag, which has semiconductor properties (Martel *et al.*, 1998). Fig. 4 indicates their structure.

Carbon nanotubes (CNTs) have particular properties and improve the mechanical, thermal, and electrical properties of nanocomposites, and therefore many studies have been performed on them recently. In a carbon nanotube, carbon atoms are arranged in a cylindrical structure. In fact, carbon nanotubes are graphite shaped like tubes. Carbon nanotubes are one of the most durable materials. This illustrates the application of carbon nanotubes as a filler in the production of polymer nanocomposites. Carbon nanotube-based composites have a high strength to weight ratio and will be widely used in industry (Meyyappan, 2004). Another very important feature of carbon nanotubes is their superconducting property. This property makes carbon nanotubes widely used in electronics. Among the important studies in the field of polymer based nanocomposites can be mentioned the study of Arash *et al.*, who investigated the mechanical properties of polymer nanocomposites reinforced with carbon nanotubes based on roughness model (Arash *et al.*, 2015). Esmaili *et al.* investigated this and found that by adding carbon nanotubes to the polymer matrix, their tensile strength and hardness increased. The results also showed that holding pressure and injection

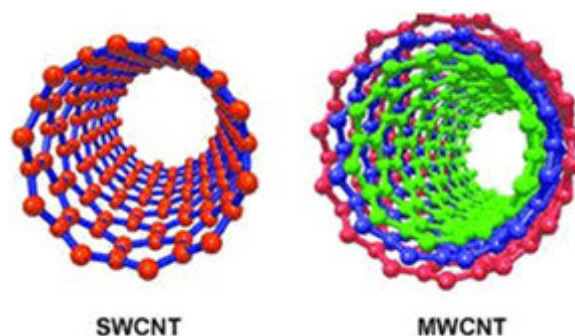


Fig. 4 Carbon nanotube, single-walled and multi-walled. Reproduced from Bhattacharyya, A., *et al.*, 2019. Simulation of Cattaneo–Christov heat flux on the flow of single and multi-walled carbon nanotubes between two stretchable coaxial rotating disks. *Journal of Thermal Analysis and Calorimetry*. 4. doi:10.1007/s10973-019-08644-4.

temperature were the next effective parameters after the weight percent of CNTs (Esmaili *et al.*, 2015). When the volume or weight fraction of CNTs in a polymer matrix exceeds a critical value, the polymer undergoes a phase shift, increasing its electrical conductivity. This critical value is called the threshold of penetration. The use of low weight percentages of carbon nanotubes as fillers has been reported for the purpose of providing electrical conductivity in polymers (Bauhofer and Kovacs, 2009).

Current researches show that carbon nanotubes (CNTs) as biomaterials have great potential for restorative medical applications. The focus of restorative medicine is on the advanced techniques used to create functional tissues, repair or replace lost tissues and organs due to wounds or diseases (Ding *et al.*, 2015). CNTs can be used as carriers for drug delivery and gene therapy, so they are suitable for therapeutic work in restorative medicine (Zheng *et al.*, 2016). The outer surface of carbon nanotubes can be functionalized for targeted drug delivery and imaging agents (Bates and Kostarelos, 2013).

Due to the carbon cylindrical structure of the nanotubes, nanoscale atoms and molecules can be encapsulated inside their interior, which can dramatically alter the properties of the polymer composite. In addition, CNTs can enclose metal, water, and molecular oxygen. For example, Reddy *et al.* functionalized multi-walled carbon nanotubes using Au or Ag nanoparticles to improve the electrical properties of the composite polymer (Reddy *et al.*, 2009).

Graphene/graphene oxides

Each of the graphite plates that are connected in a hexagonal shape is called graphene (Fig. 5). Graphene is a novel and “eco-friendly material” with a broad diversity of features that indicates significant properties which has flourished passion in the fields of material science, and continues to obtain more interest of scientists for the outlook of their potential applications for advanced engineering. Due to the high strength of the covalent bonds, graphene is very robust, despite being thin. The fourth off-screen electron (on-screen) gives the graphene a very high conductivity property. Graphene is one of the superconducting structures (Geim and Novoselov, 2010). Graphene consists of a two-dimensional nanometer-thick layers of sp²-hybridized bonded carbon atoms which is arranged as a honeycomb-like network with unique electronic and phonon transport behavior and excellent thermal conductivity, large specific surface area and great mechanical stiffness, that has been selected as one of the most propitious candidates for the next generation of polymer nanocomposites. Small loading of graphene resulted in a significant enhancement in thermal stability of the polymer matrix (Ferrari *et al.*, 2006).

Graphene, due to having high surface energy and the pi-electron freely, has many properties which leading to unique applications. The mobility of charged particles on graphene is very high. This property makes graphene a very powerful superconductor that can be used to make transistors. One of the areas where graphene is widely used is electronics applications. Particularly on touch screens, Liquid Crystal Display (LCD) and Organic Optical Diodes (OLED) (Jo *et al.*, 2012).

Many factors such as the type of graphene used and its intrinsic properties, how the graphene is dispersed in the polymer field and its interaction with the polymer and its network structure can affect the final properties and applications of graphene (Galpaya *et al.*, 2012). Martin-Gallego *et al.* compared to the mechanical and electrical properties of carbon nanotube-reinforced epoxy-based nanocomposites and graphene plate-reinforced epoxy-based nanocomposites. They reported that the mechanical performance of graphene nanocomposites increased by 50% at Young's modulus and was 5% better in strength (Martin-Gallego *et al.*, 2013).

Another very important topic about graphene is the functionalization of graphene. Functionalized graphene, in addition to being able to interact very well with polymer chains, can be present in single-layered, separated-layer plates in the polymer mass, so it can have a much greater impact on recovery and performance than normal graphene such as improvement in the physical and mechanical properties and flammability of the polymer matrix (Ramanathan *et al.*, 2008; Yuan *et al.*, 2014). Binding and grafting of macromolecules to graphene is more important than functional groups. Macromolecular chains exhibit greater thermal stability, in addition, they have a very strong space barrier to prevent re-aggregation of graphene plates. Moreover, the existence of these chains also allows graphene to become more integrated with complex organic systems. As a result, graphene functionalization with long polymer chains results in the development of new composite materials with very advanced and unique properties (Xu and Gao, 2010; Tang *et al.*, 2012). For instance, Graphene-based polyethylene nanocomposites indicate high mechanical,

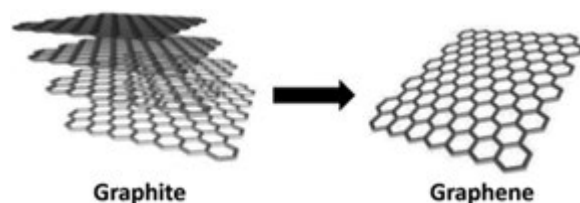


Fig. 5 Structure of graphite and graphene. Reproduced from Noked, M., Soffer, A., Arubach, D., 2011. The electrochemistry of activated carbonaceous materials: Past, present, and future. *Journal of Solid State Electrochemistry*, 15 (7–8), 1563–1578. doi:10.1007/s10008-011-1411-y.

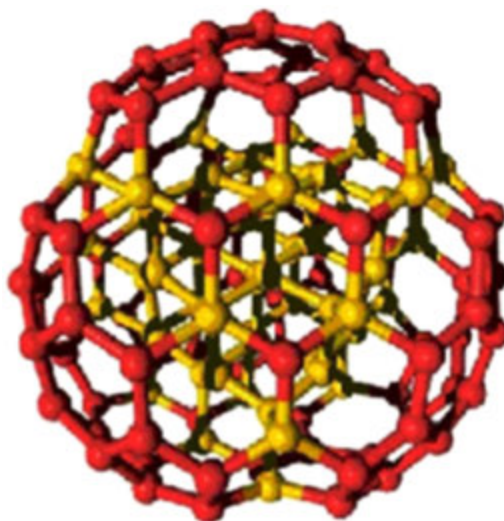


Fig. 6 Schematic of the structure of nano diamond. Reproduced from Kausar, A., 2018. Nanodiamond reinforcement in polyamide and polyimide matrices: Fundamentals and applications. *Journal of Plastic Film and Sheeting*, 34 (4), 439–458. doi:10.1177/8756087918773521.

thermal, and electrical properties rather than the raw polymer. Moreover, they prevent the passage of gases and have better flammability resistance (Becerril *et al.*, 2008; Zhao *et al.*, 2009).

It is also reported that these nanocomposites have better mechanical and electrical properties compared to nanocomposites prepared with clay and other carbon fillers (Kuilla *et al.*, 2010). Although carbon nanotubes may exhibit better mechanical properties than graphene, but in terms of electrical and thermal conductivity, graphene has better properties than carbon nanotubes (Zhao *et al.*, 2009). The chemical-physical properties of nanocomposites depend on the distribution of graphene layers to a polymer matrix and the surface bonding between the graphene layers, and polymer matrix. Pure graphene does not have good compatibility with organic polymer and does not form homogeneous nanocomposites but in contrast to graphene oxide (GO) sheets with very fine organic polymers. Unlike graphene, graphene is an oxide of electrical insulation. Pure graphene does not have good compatibility with organic polymer and does not form homogeneous nanocomposites, but graphene oxide (GO) plates are highly compatible with organic polymers and form homogeneous nanocomposites with excellent properties. Unlike graphene, graphene oxide is electrical insulation (Becerril *et al.*, 2008). Chen *et al.* used graphene oxide to improve thermoplastic polyurethane/poly lactic acid nanocomposite produced by FDM technique, the results shown that the mechanical properties and thermal stability of the produced nanocomposite using graphene oxide enhanced. Moreover, the biocompatibility properties of this nanocomposite with a type of cells, named NIH3T3, were improved (Chen *et al.*, 2017).

Diamond nanoparticles

Diamond nanoparticles are used in many polymeric nanocomposites with thermoplastic and thermoset matrix because of their unique properties. The use of these nanoparticles has improved the properties of nanocomposites such as mechanical and wear properties. The use of diamond nanoparticles, in both shape, the unmodified and modified diamond in the thermoplastic matrix has been reported to enhance mechanical properties (Mochalin and Gogotsi, 2015). Nano diamond has high hardness and strength, chemical resistance and high heat conductivity. In fact, these properties are due to the accumulation of sp^3 hybrid carbon in the cubic structure of the nanoparticle core. In addition, the nano diamond shell mainly contains sp^2 hybrid carbons and many functional groups (Fig. 6). Center Interactions of Diamond Nanoparticles with the environment depends on the surface chemistry of the nanoparticles. Therefore, the behavior of nanoparticles in different environments depends on their surface structure (Krueger and Lang, 2012; Alishahi *et al.*, 2013; Krueger, 2014; Nunn *et al.*, 2017).

One of the main problems to improve the mechanical properties, especially in nanocomposites, is the clusters and unfavorable dispersion conditions of the nanoparticles which can cause mechanical properties to decrease. One of the distinguishing features of nanodiamond compared to carbon nanotubes and other carbon nanoparticles is a large number of different functional groups on its surface. Of course, the presence of these functional groups and non-diamond carbons on the surface can sometimes increase interactions and intensify the aggregation of nanoparticles. Typically, there are various functional groups on the surface of the nanodiamond, which most of them can be used to surface covalent factorization by chemical methods (Xu *et al.*, 2005; Krueger, 2008; Mochalin *et al.*, 2012).

Surface modification of nanoparticles is accomplished with the two general goals of reducing agglomeration and enhancing nanoparticle-polymer interactions. For example, in a study, by silanization of diamond nanoparticles, surface interactions with polydimethylsiloxane polymer were increased based on the results of rheumatic tests. Accordingly, modified diamond nanoparticles have been proposed as a suitable option to enhance the mechanical properties of this polymer (Hajiali and Shojaei, 2016).

Numerous studies have been carried out on diamond nanoparticles as reinforces in thermoplastic matrices. Even at low weight percentages and without superficial modification, nano-diamonds have shown to be capable of reinforcing these matrices. For example, the addition of 0.25 wt% Of nanodiamond in the polyurethane-2-hydroxy methacrylate matrix has led to an increase in the glass transition temperature and the Young's modulus. This increase is explained by the reaction between the carboxyl groups of the nanodiamond surface with the isocyanate groups during polymerization. The research shows that even without surface modification, diamonds can enhance the properties of nanocomposites (Bershtein *et al.*, 2008). Numerous studies have been done on epoxy-nanodiamond nanocomposites. To further enhance the mechanical properties of this polymer and to investigate the amount of nano-diamond reinforcement, epoxy-nano-diamond composites were made by up to 35% by volume percentage of nanoparticles. Young's modulus and hardness of these composites increased by 300% and 700%, respectively, as Young's modulus increased to 20 GPa. At such a large percentage of nanodiamond, the nanocomposite can be considered as a network of nanodiamond with the polymer as a bond between them. Direct contact of diamond nanoparticles at such a Volume percentage of nanoparticles also enhances the thermal conductivity properties (Ayatollahi *et al.*, 2012; Rakha *et al.*, 2013; Aris *et al.*, 2015).

Summary

Polymer nanocomposite materials exhibit advantageous physical properties. These include improved thermal stability, flame retardancy, enhanced barrier properties, and improved mechanical properties. Commercially, the developments in polymer nanocomposites are resulting in their increased usage. The combination of improved properties, including weight reduction and low cost in the final product, provide important commercial applications in the transport sector.

The range of applications as noted in this article are many. Nano carbons and nanoceramics have tremendous potential for variety of application, where it could be used to enhance the composite materials in industry. Research has revealed that dispersing a small amount of nanomaterials specially graphene, CNTs and nanoclay in polymers can significantly improve many properties of the resulting composites, such as tensile strength and elastic modulus, electrical and thermal conductivity, thermal stability, gas barrier, and flame retardancy. Based on these multifunctional properties, polymer matrix nanoceramic or nanocarbon composites are promising as both structural and functional composites, with the integration of functionalities within the industry. Here also, during the fabrication of polymer nanocomposites, one of the challenges that engineers and researchers face is the lack of new methods of large-scale production of polymer nanocomposites. Compared to traditional manufacturing technologies, additive manufacturing offers many exclusive advantages in terms of material efficiency, straightforward operating style, and better design flexibility.

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Investigations of Graphene Reinforced Acrylonitrile-Butadiene-Styrene Matrix Prototypes Produced Via Functional Deposition Modeling (FDM)

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Introduction

In the past three decades significant research efforts have been focused on the development of feed stock filaments for commercial 3D printers (Boparai *et al.*, 2016). A large variety of thermoplastics and thermoplastic composite matrix materials are widely available with acceptable thermo-mechanical properties (Singh *et al.*, 2016; Garg and Singh, 2017). These thermoplastic composites based prototypes have acceptable mechanical properties, but thermal and electrical properties limit their application as sensors and actuators (Sandhu and Singh, 2017; Singh *et al.*, 2018).

The Gr is two-dimensional (2D) carbon nanostructure (Zhu *et al.*, 2010), with good mechanical/thermal/chemical, and electrical properties (Dikin *et al.*, 2007; Geim and Novoselov, 2007). Gr also possess exciting electronic and optoelectronic properties (Zhu *et al.*, 2010) and has attracted much attention for development of sensors and actuators (Geim, 2009). Commercially the Gr layers are mechanically exfoliated from graphite (Menczel *et al.*, 2009; Kuilla *et al.*, 2010; Novoselov *et al.*, 2004). Being 2D system, Gr represents highly efficient electromechanical system (He *et al.*, 2012) resulting into extremely sensitive conductance of Gr (Soldano *et al.*, 2010; Zheng *et al.*, 2010). The Gr has potential as sensor material in typical bio-medical applications (Abergel *et al.*, 2010). In addition to Gr, chemically modified Gr/ its composites with metal/metal oxides/polymers are also acceptable as sensor materials (Amin and Bid, 2014; Mao *et al.*, 2012; Deng *et al.*, 2012; Kaniyoor *et al.*, 2009; Kang *et al.*, 2010). In this article experimental investigations have been reported for porosity and Shore hardness of 3D printed (using FDM) functional prototypes prepared from ABS-Gr blended filament for typical sensor applications, as an extension of previously reported studies (Sandhu and Singh, 2019; Singh *et al.*, 2017). Like other additive manufacturing (AM), FDM also uses layer by layer fabrication approach (Wong and Hernandez, 2012). It utilizes a temperature-controlled extruder and store the semi-liquid polymer onto a stage. The feed stock filament is moved by rollers to drive the semi-molten thermoplastic material. The process parameters of each layer depend on the prior inputs in the slicing software. Some of the input parameters are: FDM head speed, roller speed, in-fill density (expressed in %), and deposition pattern etc. Since the commercially available feed stock filament materials used for FDM, are having poor thermal/electrical properties, in recent past some efforts were made to develop filament material that is conductive in nature and execute good applications for making sensors (Singh *et al.*, 2017). As a matter of fact porosity is undesirable, which comes into picture when any thermoplastic material is under cooling stage/ softening stage which entraps air. Now days the carbon based materials (such as Gr) are also of great interest due to high surface area/low density/exceptionally good electrical conductivity/chemical inertness (Xu *et al.*, 2010; Sheng *et al.*, 2011; Kondratowicz *et al.*, 2015) and low fabrication cost (Xia *et al.*, 2014). Along with this other important property to be considered for making ABS-Gr based sensors

Table 1 Observations for MFI

ABS: Gr (wt%)	MFI of mechanically blended thermoplastic composite (g/10 min)	MFI of chemically blended thermoplastic composite (g/10 min)
50:50	0.82 ± 0.2	1.63 ± 0.2
60:40	1.62 ± 0.2	2.27 ± 0.2
70:30	2.20 ± 0.2	3.20 ± 0.2
80:20	2.46 ± 0.2	3.94 ± 0.2
90:10	2.51 ± 0.2	4.12 ± 0.2

Table 2 Input parameters

Input parameters	Symbolic representation	Levels (0/1)
Blending process	A	Chemical + mechanical (Level 0) Mechanical (Level 1)
Proportion of ABS: Gr (wt%)	B	75/25 (Level 0) 90/10 (Level 1)
Infill density (%)	C	50% (Level 0) 100% (Level 1)

Table 3 Control log of experiment as per historical data approach

Experiment No.	A	Level	B	Level	C	Level
1	Chemical + mechanical	0	75/25	0	50	0
2	Chemical + mechanical	0	75/25	0	100	1
3	Chemical + mechanical	0	90/10	1	50	0
4	Chemical + mechanical	0	90/10	1	100	1
5	Chemical + mechanical	0	75/25	0	50	0
6	Chemical + mechanical	0	75/25	0	100	1
7	Chemical + mechanical	0	90/10	1	50	0
8	Chemical + mechanical	0	90/10	1	100	1
9	Mechanical	1	75/25	0	50	0
10	Mechanical	1	75/25	0	100	1
11	Mechanical	1	90/10	1	50	0
12	Mechanical	1	90/10	1	100	1
13	Mechanical	1	75/25	0	50	0
14	Mechanical	1	75/25	0	100	1
15	Mechanical	1	90/10	1	50	0
16	Mechanical	1	90/10	1	100	1

Table 4 Observations for porosity of tested samples

Experiment No.	A	B	C	Porosity (%)	Shore D hardness
1	Chemical + mechanical	75/25	50	12.05	53.6
2	Chemical + mechanical	75/25	100	21.76	66.3
3	Chemical + mechanical	90/10	50	19.02	55.7
4	Chemical + mechanical	90/10	100	22.26	67.4
5	Chemical + mechanical	75/25	50	12.04	53.5
6	Chemical + mechanical	75/25	100	21.75	66.4
7	Chemical + mechanical	90/10	50	19.02	55.6
8	Chemical + mechanical	90/10	100	22.25	67.3
9	Mechanical	75/25	50	22.61	52.4
10	Mechanical	75/25	100	31.78	63.1
11	Mechanical	90/10	50	27.58	59.6
12	Mechanical	90/10	100	44.84	66.0
13	Mechanical	75/25	50	22.60	52.3
14	Mechanical	75/25	100	31.76	63.1
15	Mechanical	90/10	50	27.54	59.5
16	Mechanical	90/10	100	44.82	66.1

is hardness. The present study reveals macro model to control porosity and Shore D hardness while 3D printing of ABS-Gr based thermoplastic matrix (in which Gr was prepared by exfoliation of graphite in organic solvents with addition of naphthalene) as suggested in previous studies (Singh *et al.*, 2017). The lump of composite material was crushed mechanically and fed mechanically to twin screw extruder (TSE). The Thermo Scientific HAAKE Mini CTW (Make: Germany) was used for filament preparation. The fixed parameters selected were: rotation speed 200 rpm; load 10 kg at 180°C (Singh *et al.*, 2017). Final diameter of the extruded filament was selected as 1.75 ± 0.10 mm (based upon available open source FDM setup). For mechanical blending Gr and ABS were directly fed into the hopper of TSE. Finally the polymer composite filament was prepared for FDM.

Experimentation

The primary recycled ABS (with melt flow index (MFI) 2.9 g/10 min as per ASTM D 1238-73) was procured Batra Polymers, Ludhiana (India). The graphite powder (thermal conductivity: 2–90 W/m K) was supplied by Bharat Graphite Pvt. Ltd. (Ludhiana, India). For addition of Gr in ABS the MFI values were calculated (Table 1).

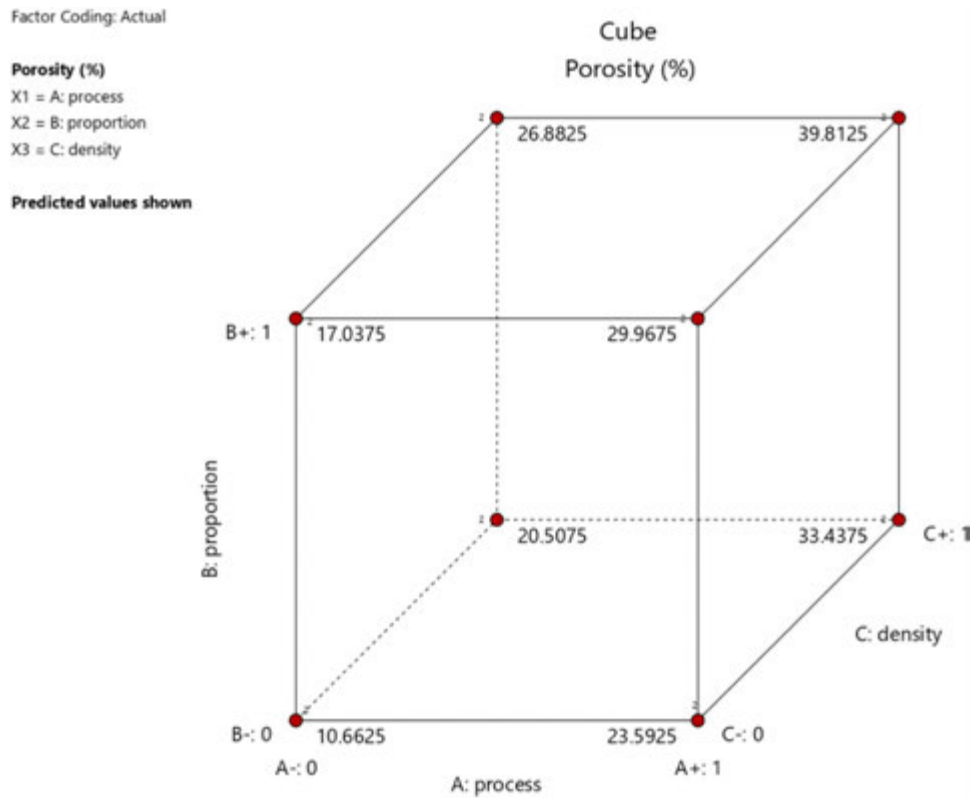
Based upon Table 1, experiment was conducted with 25 g Gr blended with 75 g ABS and 40 g acetone. The resulting proportion of Gr was calculated as under:

$$= \left[\frac{25 \text{ g(Gr)}}{75 \text{ g(ABS)} + 40 \text{ g(Acetone)}} \times 100 \right] = 21.7\% \quad (1)$$

Table 5 ANOVA for Porosity

Source	SS	DF	MS	F-Value	P	
Model linear	1219.00	3	406.33	38.41	< 0.0001	Significant
A	668.74	1	668.74	63.21	< 0.0001	
B	162.56	1	162.56	15.37	0.0020	
C	387.70	1	387.70	36.64	< 0.0001	
Residual	126.96	12	10.58			
Lack of Fit	126.96	4				
Pure Error	0.0000	8				
Cor Total	1345.96	15				

Note: SS: Sum of Squares, DF: Degree of freedom, MS: Mean Square, F: Fisher's, P: Probability.

**Fig. 1** Porosity (%) variation with respect to input parameters (A, B and C).**Table 6** ANOVA for Shore D hardness

Source	SS	DF	MS	F-Value	P	
Model linear	475.69	3	158.56	54.41	< 0.0001	Significant
A	0.9025	1	0.9025	0.3097	0.5881	
B	44.22	1	44.22	15.18	0.0021	
C	430.56	1	430.56	147.75	< 0.0001	
Residual	34.97	12	2.91			
Lack of Fit	34.97	4	8.74			
Pure Error	0.0000	8	0.0000			
Cor Total	510.66	15				

Factor Coding: Actual

Shore D hardness (Shore D)

X1 = A: process

X2 = B: proportion

X3 = C: density

Predicted values shown

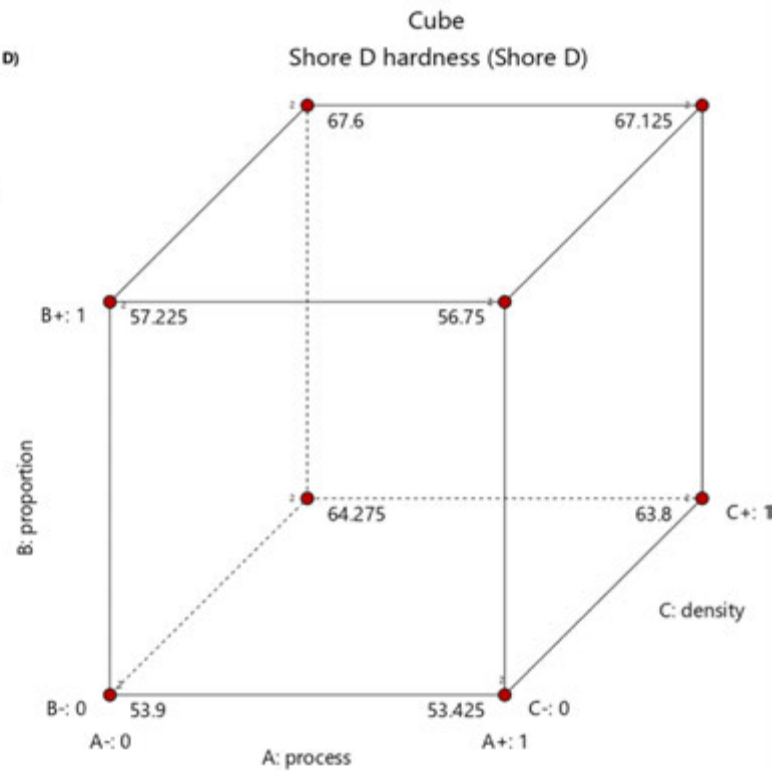


Fig. 2 Shore D hardness variation with respect to input parameters (A, B and C).

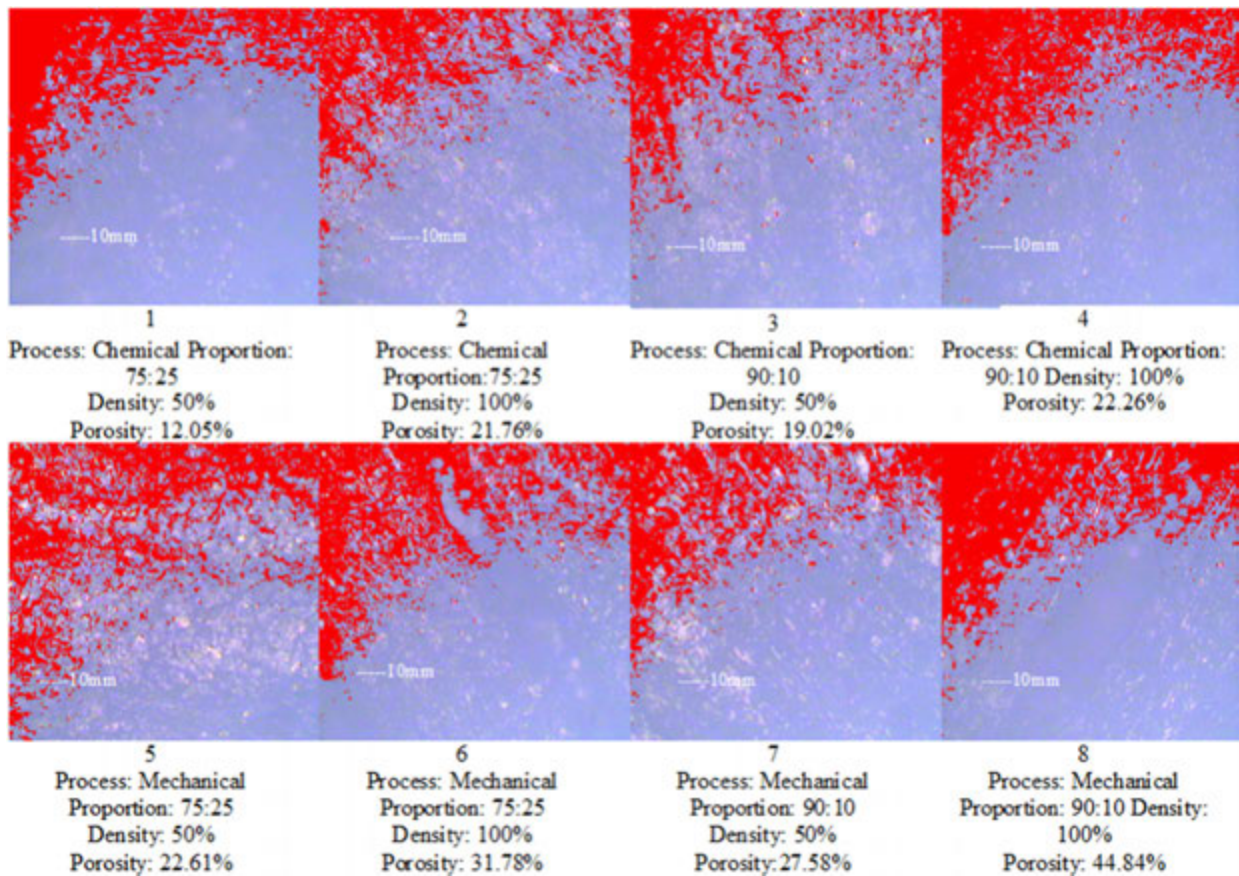


Fig. 3 Optical micrographs of ABS-Gr chemically and mechanically blended samples (at $\times 100$).

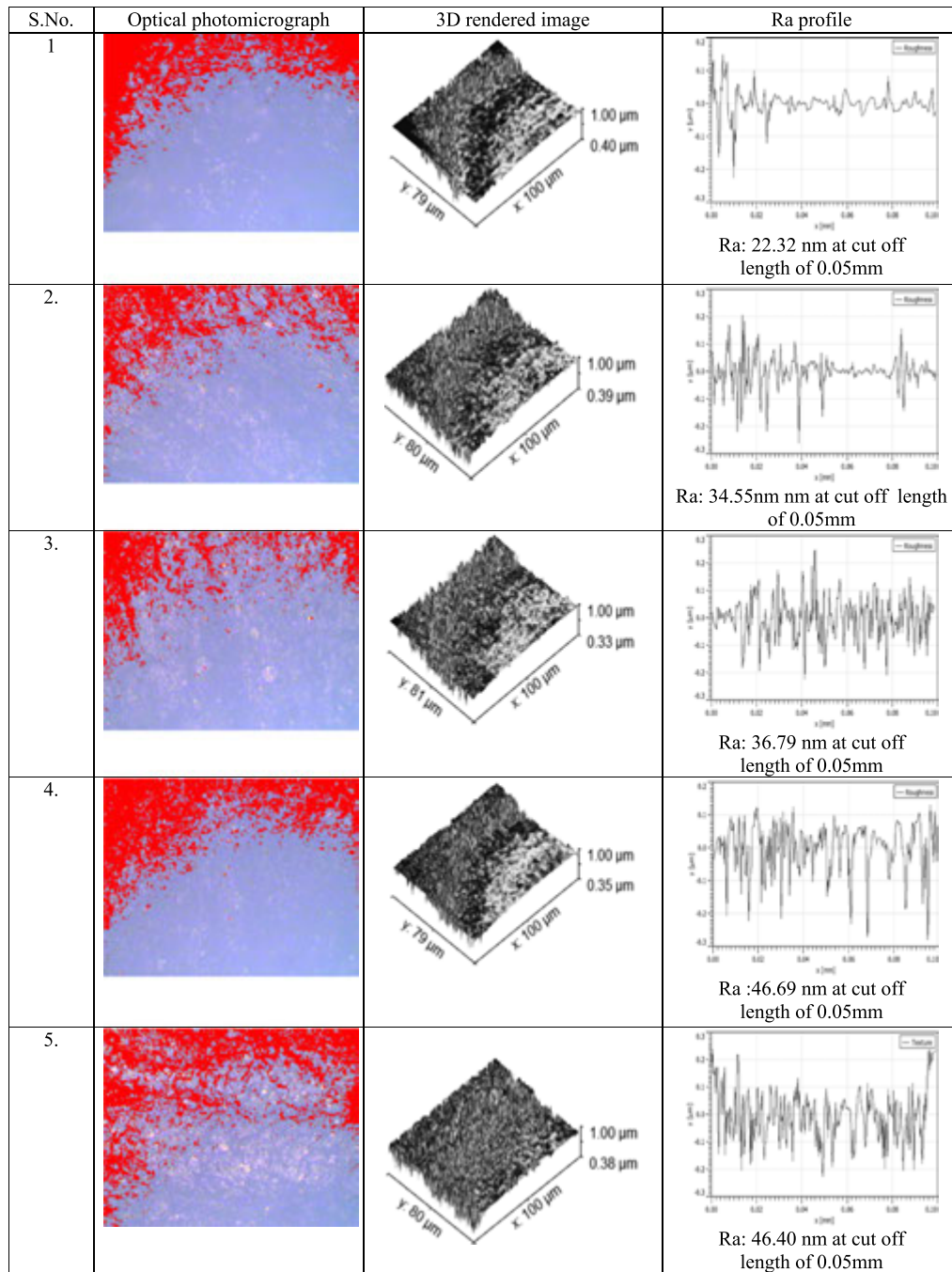


Fig. 4a 3D surface profiles and Ra profile (as per Fig. 3).

Similarly for another proportion of 90 g ABS and 10 g Gr dispersed in 40 g acetone, the resulting weight proportion of Gr was 7.69% (Singh *et al.*, 2017).

For further experimentation these two proportions were selected to prepare filament on TSE for possible processing on open source FDM (Model: Accucraft i250 FDM printer, Make: Divide By Zero, Pune, India). The fixed parameters of FDM were: honeycomb pattern, nozzle diameter 0.4 mm, layer height 0.4 mm, nozzle temperature 230°C; bed temperature 55°C. Table 2 shows the input parameters selected in these investigations. Based upon Table 2, Table 3 shows control log of experiment as per historical data approach.

Based upon Table 3, the porosity was calculated based upon optical photomicrographs at $\times 100$ as per ASTM E 2015-04(2014) and Shore D hardness was noted.

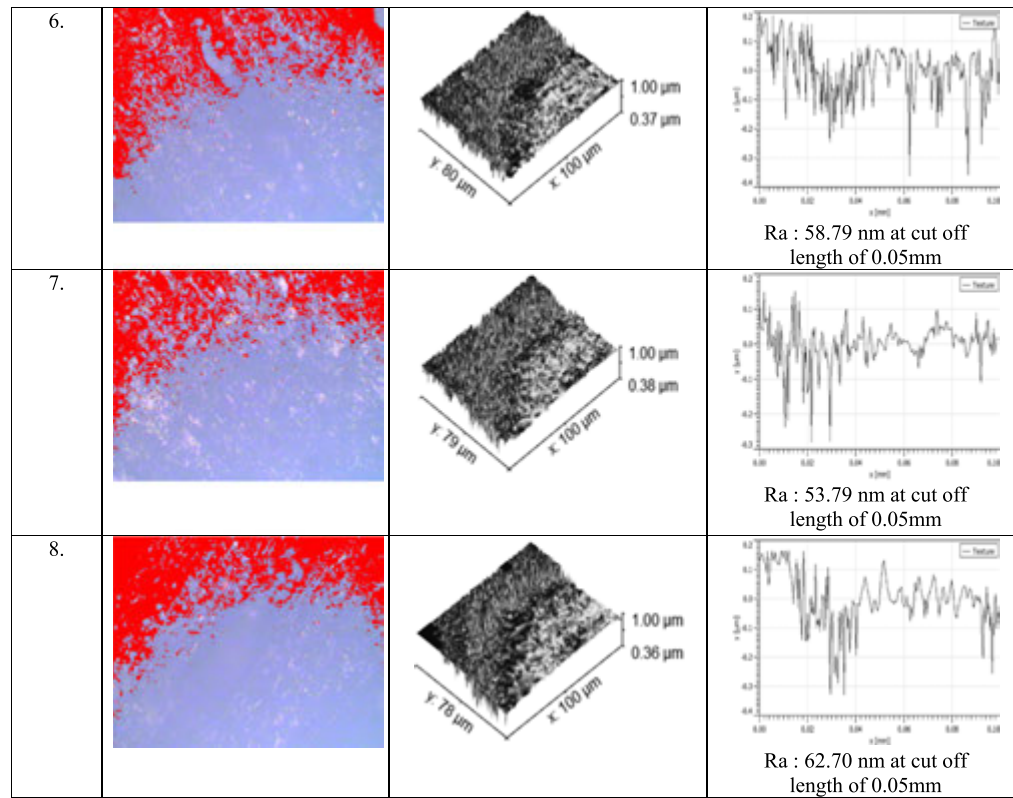


Fig. 4b Continue.

Results and discussion

For porosity and surface hardness analysis (based upon Table 3) experiments were conducted and it was noticed that standard error value is less than 5% as per ISO/IEC guide 98-3-1 (Table 4).

Based upon Table 4, analysis of variance (ANOVA) has been conducted for porosity and Shore D hardness. It has been suggested that model of experimentation as per outcomes of porosity is significant at 95% confidence level (Table 5) as P value is <0.05 . As observed from Table 5, blending process (A) and infill density (B) are significant for controlling porosity.

The model F-value of 38.41 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C are significant model terms.

Final equation in terms of coded factors:

$$\text{Porosity} = +25.24 + 6.46A + 3.19B + 4.92C$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. Further based upon Table 4, Fig. 1 shows variation of porosity (%) with respect to input parameters (A, B and C) in cube form.

Further based upon Table 4, Table 6 shows ANOVA for Shore D hardness.

The model F-value of 54.41 implies the model is significant. In this case B, C are significant model terms.

Final equation in terms of coded factors:

$$\text{Shore D hardness} = +60.51 - 0.2375A + 1.66B + 5.19C$$

Further based upon Table 4, Fig. 2 shows variation of Shore D hardness with respect to input parameters (A, B and C) in cube form.

Fig. 3 shows porosity (%) data captured through optical microscope at $\times 100X$ as per ASTM E 2015-04(2014). As observed from Fig. 3 for sample 1, minimum porosity was observed, which may be used for making ABS-Gr based sensors with better thermal as well as electrical properties. These observations are average values of repeated experiments (based upon historical data, Table 3). Further based upon Fig. 3, Fig. 4 shows 3D rendered images and corresponding Ra profiles for comparison.

As observed from Fig. 4 with rendered 3D images (which shows uniform grain distribution) and Ra profile the results are in line with porosity observations (as per Fig. 3). For example: In case of sample at S.No. 1 (Fig. 3) minimum porosity was observed and corresponding Ra value is also minimum (see Fig. 4, S.No.1).

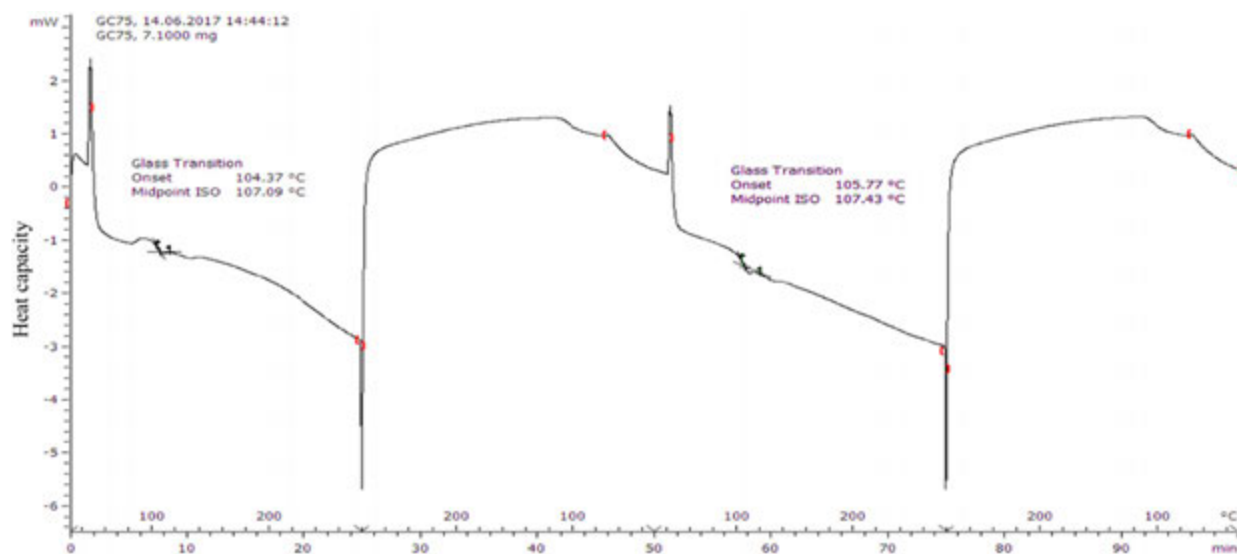


Fig. 5 Heat capacity vs. Temp./time (for chemically blended sample with proportion 75:25% and 100% infill density).

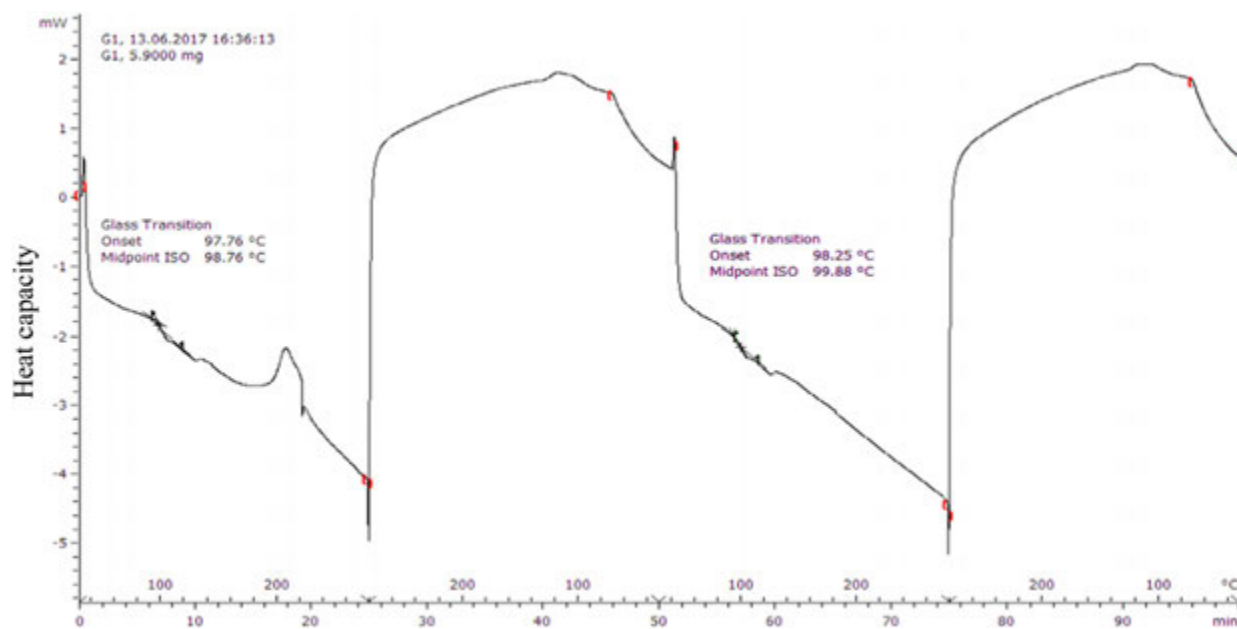


Fig. 6 Heat capacity vs. Temp./time (for mechanically blended sample with proportion 75:25% and 100% infill density).

Further to understand the thermal stability of 3D printed samples; commercial DSC setup "METTLER TOLEDO model DSC3 with STAR[®](SW 14.00)" has been used to examine the glass transition temperature (T_g) of two different methods (chemical and mechanical). The temperature range was set from 30°C to 280°C at an increasing rate of 10K/min, in the presence of N_2 gas at flow rate 50 ml/min. Figs. 5 and 6 shows the DSC graphs for chemically and mechanically blended samples. As shown in Fig. 5, small drop was observed for T_g in the first heating cycle (104.37°C), while 105.77°C during the second heating cycle. It should be noted that T_g of virgin ABS is 105°C.

Similarly for mechanically blended sample with proportion 75:25% and 100% in-fill density, a small drop occurred in the curve having value 97.76°C shows T_g in the first heating cycle, while 98.25°C during the second heating cycle (Fig. 6). The T_g shows that the observed values in chemically blended samples are much closer to the T_g of ABS i.e., 105°C while in case of mechanically blended samples the temperature range is quite far. However these samples are thermally stable and can be successfully recycled.

Conclusions

The FDM feed stock filament with ABS-Gr matrix has been successfully prepared through mechanical mixing and chemical mixing. Further feed stock filament has been used for preparing functional prototypes. Finally the porosity and shore hardness of the functional prototypes have been optimized. The following conclusions can be drawn from the present study. For the process of blending Gr in ABS matrix, the proportion of ABS: Gr (wt%) and infill density (%) are the significant parameters for final part porosity. Whereas for Shore hardness, the proportion of ABS: Gr (wt%) and infill density (%) are the significant parameters. Based upon parametric optimization for porosity and Shore hardness, better electrical and thermal conductivity can be attained while optimizing Shore hardness values. Finally based upon thermal stability, Ra values and 3D rendered images of photo-micrographs, it can be concluded that the functional prototypes are sufficiently physically robust to be used as sensing elements.

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Processability of High Metal and Ceramic Concentration Compounds

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Introduction

Highly concentrated metal and ceramic compounds are widely employed in compounds for powder injection molding, where the attributes of powder metallurgy (e.g., low cost, simplicity, and flexibility of composition selection) with those of plastic injection molding (e.g., easy-to-manufacture complex parts and rapid production) are met. Currently, the demands on characterization of these materials are strengthened by merging powder injection molding with additive manufacturing (Williams, 2018).

As the processability of the metal powder filled compounds is evaluated through their flow performance, the crucial point is their rheological description. It starts with the necessity to set up optimum powder loading and characteristics in terms of shape, size and particle size distribution, which means always to find a compromise among the demands of the particular processing steps – mixing (preparation of the processed compound where a polymer binder bonds powder particles), injection molding or 3D printing, debinding, and sintering.

Ceramic powders most often employed for highly filled compounds are oxides of aluminum and zirconium. Metal powders, which are in general coarser, include stainless steels as 316 L and 17–4 pH well established in medical and automotive sectors, nickel-chromium based superalloys, sintered carbides, and, in the last decade, increasingly also reactive powders as titanium and its alloys (German, 2013). The critical processing powder factors are contradictory, and therefore the compromising solution must be found as there exists no remedy in the particular processing steps how to cope with the shortcomings in the preceding steps.

As there are excellent reviews on rheological properties of highly concentrated compounds reported relatively recently (e.g., Rueda *et al.*, 2017), this article will address the issues, which remain open. These include: viscosity data evaluation, applicability of available rheological models, and intercepting effect of pressure. The studies available at present are devoted mainly to the particular applications, whereas the reliable and fundamental approaches are missing. The severe failures of current investigations lay in both the measurements of these highly complex materials, and the evaluation of data, where the majority of research employs rheological models for rheologically simpler materials such as pure polymer melts.

The classical trial-and-error processing has no longer rationale in fundamental research. However, while the simulation of debinding and sintering steps is well established (e.g., by Sahli *et al.* (2018)), this has not been the case for part-forming step, where the rheological description of the used feedstocks faces instabilities and serious challenges (Hausnerova *et al.*, 1999; Honek *et al.*, 2002), and the discrete approximation of rheological parameters introduces errors in data fitting (Filip *et al.*, 2020).

Rheological Specifics of Highly Concentrated Compounds

Viscosity (resistance against flow) is usually evaluated as a function of rate of shear deformation and temperature. Nevertheless, the situation is much more complex for metal and ceramic compounds as further factors playing a considerable role are: high concentration of powder, particle geometry, binder composition, a way of feedstock preparation, interactions among binder components and powder, participation of surfactants, flow channel geometry and surface properties, and feedstock-flow channels wall interactions. Just for an illustration, the following references document the individual analyses.

The investigation was focused on the effect of mixing process parameters (powder loading, rotor speed and mixing temperature) by means of which viscosity was evaluated (Abdullahi *et al.*, 2017). The effects of particle size, flow activation energy and the moldability index on the rheology of the feedstock were studied in detail by Claudel *et al.* (2017). Quantitative analysis of the relationship between the material structure (powder characteristics) and flow properties of highly filled compounds was proposed by Hausnerova and Zidek (2016); the model parameters are the powder particle-size distribution and its volume fraction in a compound. Later, Park and Park (2018) analyzed the relationship between viscosity and powder particle size, using also an image-processing method to quantify the inter-particle distances.

Multi-component character of binders makes the rheological description of compounds even more uneasy, and in spite of relatively low concentrations of surfactants, their presence significantly alters the rheological characteristics of the feedstocks as a bulk (Fareh *et al.*, 2016). A powder with different combinations of binder systems and a binder system with different combinations of powder systems were investigated with a combined experimental and simulation approaches by Kate *et al.* (2013). In Park *et al.* (2018) viscosity, shear sensitivity and temperature sensitivity were closely related to the molecular weight difference in binder composition.

However, other important aspects as evaluation of flow data including a wall slip, application of suitable models to their fitting, and considering a pressure effect during high-pressure processing as injection molding are still rather omitted, and thus discussed in the following sections.

Viscosity Evaluation

The proper description of rheological behavior (a determination of true viscosity) is tightly interlaced with respecting Bagley and Weissenberg-Rabinowitsch corrections (Bagley, 1957; Rabinowitsch, 1929). The Bagley correction is used to compensate different capillary geometries regarding entrance pressure and outlet extension. The Weissenberg-Rabinowitsch correction is used to compute the actual velocity (non-parabolic profile) and thus, shear rate distribution in a non-Newtonian fluid (concentrated compound). Further, the determination of true rheological characteristics might be complicated by the presence of the wall slip phenomenon. Ardakani *et al.* (2011) found that no-slip condition leads to inaccurate simulation even in a simple pipe flow. As an example, a thorough modeling study of injection molding process with various molding parameters and complex material characterization carried out by He *et al.* (2016) showed measured powder concentration within injected feedstocks approximately 5%–6% lower than simulated due to a no-slip condition set up as a boundary condition.

Wall slip evaluation

During processing of high metal and ceramic concentrated compounds, a contact between feedstock and channel walls results often in the occurrence of so called slip layer (Kalyon and Aktas, 2014; Soltani and Yilmazer, 1998) containing only the pure binder system while the feedstock as a bulk material occupies most of the flow region (Ramamurthy, 1986; Kalika and Denn, 1987). In this respect, a method to determine wall slip layer thickness instead wall slip velocity was proposed by Kwon and Ahn (1995). Choi and Kim (2011) have shown that an implementation of a wall slip into flow simulations is necessary for channel diameters smaller than 10 μm . Thus, the wall slip correction model gains even higher importance if micro injection molding is simulated. Recently, the slip of the micro-powder injection molding of zirconia feedstock was considered by Liu *et al.* (2018a) with the clear conclusion that it cannot be ignored in numerical simulations. In the following work Liu *et al.* (2018b) supported this finding when compared the simulations of temperature, viscosity and pressure gradient distributions during mold filling including/excluding wall slip.

Wall slip is quantified with the help of Mooney (1931) correction developed for a pressure driven flows, where a set of capillaries of different radii are employed to estimate the slip corrected apparent shear rate from the extrapolation of apparent shear rate vs. inverse radius plots down to inverse radius tending to zero. However, in case of concentrated suspensions, the Mooney plots are often non-linear and/or have negative intercepts on the apparent shear rate axis. Further limitation has been recently risen up by Mazzanti and Mollica (2017) who have shown that the gap sizes applicable for Mooney analysis have the upper limit for concentrated compounds, since the slip is substantially promoted by a low pressure.

Geometrical arrangement of the capillary dies in the capillary rheometers participates significantly in the obtained rheological characteristics. An application of flat or conical dies changes both slip layer thickness and slip velocity. The literature comparing flat and conical dies in connection with wall slip effect is rather scarce. Changes in pressure drop with different capillary angles during extrusion were tested by Ardakani *et al.* (2011), Liang (2001a,b) and Sanetnik *et al.* (2018). It was found that under constant pressure, shear rate increased with higher capillary entrance angle.

Also, a chemical nature of the dies has an effect on a wall slip velocity. Stainless steel dies, which are mostly used for processing tools, are much more prone to a wall slip than ceramic or glass dies (Chen *et al.*, 1993) due to their relatively small work of adhesion, and also a smooth capillary surface in comparison to a rough surface of e.g., aluminum. According to Mnekbi *et al.* (2010), formation of low molecular layer will be suppressed, if particles can move into the groove of a rough wall solid. Recently, it has been confirmed for high concentration metal and ceramic compounds, where the slip velocity was evaluated using rectangular slit dies adapted to online extrusion rheometer (Sanetnik *et al.*, 2019).

Empirical Constitutive Modeling

The models can be separated into two groups. The first one works with the model fitting (adjustable) parameters with no explicit relation to suspension characteristics. The participation of individual characteristics of the applied materials is implicitly projected onto the individual parameters with no apparent interrelations. The models representing the second group explicitly exhibit the material and process characteristics such as concentration of solid fraction, its maximal value, particles distribution, influence of binder components.

Models Without Participation of Suspension Characteristics

Complexity of concentrated compounds prevents from an application of differential and integral constitutive models used for instance in a description of flow behavior of polymer melts (majority of them based on molecular arguments). In the case of the high concentrated compounds proceeded with extrusion or injection molding an application of empirical or phenomenological models absolutely dominates. Contrasting to the fact that shear stress behavior is continuous across the interface in two-phase flow in comparison with a course of shear rate (see Lomellini and Ferri (2000)) usage of the models where viscosity depends on shear stress is really seldom. In the following choice of the constitutive equations (models) the stress-dependent viscosity is presented and it is shown that such models not exceptionally preceded the ones with shear rate-dependent relations.

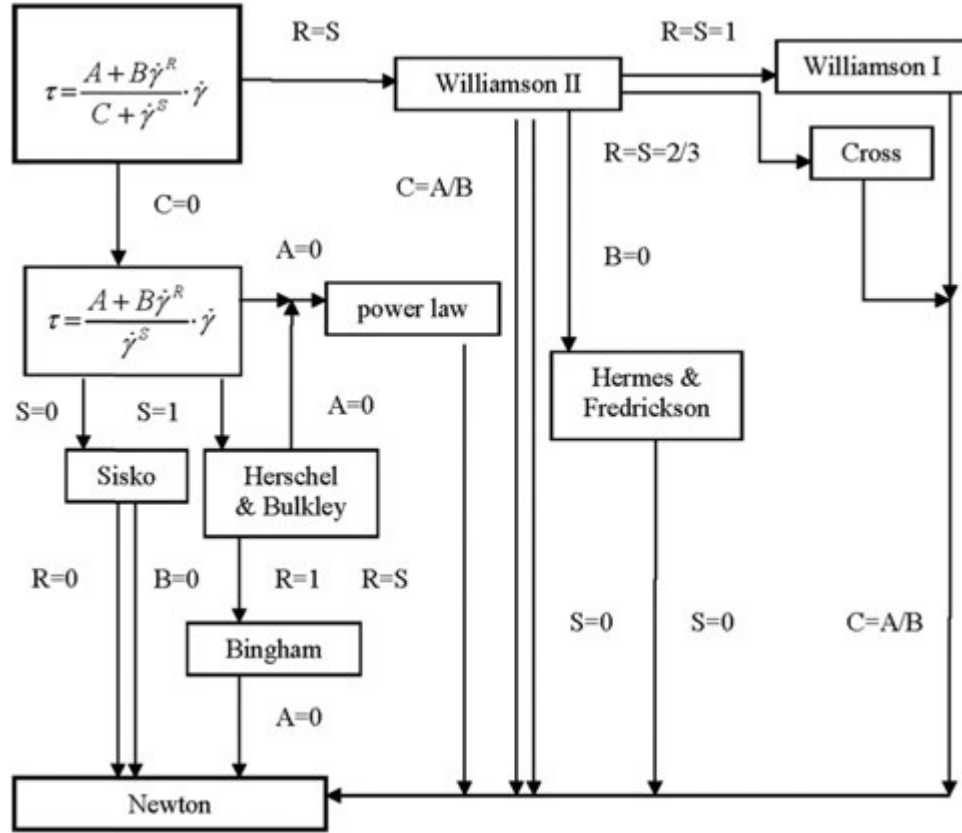


Fig. 1 'Genesis' of the basic rheological models.

The introduction of the classical models (and still often used due their efficiency) describing flow of non-Newtonian materials (viscosity is not dependent on temperature and pressure only) dates back to the 1920s of the last century. These models (both purely viscous and viscoplastic) involve only two to three adjustable parameters, thus ensuring uniqueness of their values in the process of experimental data fitting. Two classical two-parameter (2P) models, i.e., the power-law (Ostwald-de Waele) model (Ostwald, 1929)

$$\tau = K|\dot{\gamma}|^{n-1} \cdot \dot{\gamma} \quad (1)$$

and the Bingham model (Bingham, 1922)

$$\tau = \left(\eta_0 + \frac{\tau_0}{|\dot{\gamma}|} \right) \dot{\gamma} \quad (2)$$

were combined into the 3P Herschel-Bulkley one (Herschel and Bulkley, 1926)

$$\tau = \left(K|\dot{\gamma}|^{n-1} + \frac{\tau_0}{|\dot{\gamma}|} \right) \dot{\gamma}. \quad (3)$$

In this pioneer period there appeared also two 3P empirical constitutive models, specifically the Williamson model (Williamson, 1929)

$$\tau = \left(\eta_\infty + \frac{A}{B + |\dot{\gamma}|} \right) \dot{\gamma}. \quad (4)$$

and the Peak-McLean model (Peek and McLean, 1931)

$$\tau = \left(a + \frac{1}{b + c\tau} \right) \dot{\gamma}. \quad (5)$$

The functional forms of both models are identical, the only difference is in expressing the viscosity term: either depending on shear rate or shear stress. Fig. 1 introduces an algebraic connection among the basic models. It confirms that usage of the algebraically simple relation (the left upper corner) can responsibly model a vast range of non-Newtonian materials starting with the power-law behavior and applying for instance the Cross model as well. As apparent, all roads lead to the Newtonian behavior.

The same possibility of choice was presented in the second period of publishing empirical models, i.e., 1950s and 1960s, when first the 3P Reiner-Philippoff model (Philippoff, 1935; Reiner, 1949) was introduced

$$\tau = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \tau^2/\tau_0^2} \right] \dot{\gamma}, \quad (6)$$

later generalized by the 4P Meter model (Meter and Bird, 1964)

$$\tau = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\tau/\tau_c)^m} \right] \dot{\gamma} \quad (7)$$

and the 5P model (Van Vazer *et al.*, 1963)

$$\tau = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + a\tau + b\tau^m} \right] \dot{\gamma}, \quad (8)$$

Finally it was rewritten to the 4P Cross model (Cross, 1965)

$$\tau = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (K|\dot{\gamma}|)^m} \right] \dot{\gamma}. \quad (8)$$

The same number of parameters has also the 4P Carreau model (Carreau, 1968)

$$\tau = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{\left(1 + (\lambda|\dot{\gamma}|)^2\right)^{(1-n)/2}} \right] \dot{\gamma}. \quad (9)$$

These models exhibit the following attributes:

- simple algebraic form,
- limited number of parameters (up to 4) ensuring their unambiguous determination,
- monotonous passage from the first - upper (lower) - Newtonian plateau η_0 to the second - lower (upper) - Newtonian plateau η_{∞} ,
- "symmetry" of the viscosity profile (i.e., the drop-off in viscosity from η_0 is mirrored by its rapid levelling-off towards η_{∞}); in other words, there is a strict reciprocity between convexity and concavity,
- each parameter controls a specific part of viscosity curve (first and second Newtonian plateaux, width and steepness of an interplateaux region, yield stress),
- in the case of viscoplastic models the additive term τ_0 (representing yield stress - up to which no deformation is detectable from outside) causes - as a singular term - apart from numerical problems also the physical one: shear rate tending to zero results in infinite value of viscosity (an ordinate (vertical axis) is a tangent of a viscosity curve at zero shear rate),
- described materials are supposed to be single-phase and homogeneous; if these models are applied to other materials there is no possibility to reflect this change.

The fact that behavior of materials used in practice generally do not meet all of the above attributes and also an approach eliminating singularities is preferred, was reflected in the 1970s and 1980s in completely new approaches to empirical modeling. In the following the individual advances are discussed in more detail.

Elimination of the yield stress τ_0 as a singular term in viscoplastic models

Consecutively there appeared four different approaches how to suppress a singular term τ_0 in the Bingham and Herschel-Bulkley models.

- (1) The Vocadlo model (Parzonka and Vocadlo, 1968) sometimes denoted as the Robertson-Stiff model (Robertson and Stiff, 1976)

$$\tau \left[K|\dot{\gamma}|^{\frac{n-1}{n}} + \left(\frac{\tau_0}{|\dot{\gamma}|} \right)^{\frac{1}{n}} \right]^n \dot{\gamma} \quad (10)$$

incorporates yield stress term in such a way that shear viscosity attains a finite value for shear rate approaching zero (see Fig. 2) and moreover, its form enables solutions of some flow problems in a (semi)analytical form (Filip and David, 2003).

- (2) Bercovier and Engelman (1980) eliminated singularity at $\dot{\gamma} = 0$ by inserting a negligibly small additive term ε into the denominator of the Bingham model

$$\tau = \left[\eta_0 + \frac{\tau_0}{(|\dot{\gamma}| + \varepsilon)^{1/2}} \right] \dot{\gamma} \quad \text{for } \tau^2 \geq \tau_0^2; \quad \dot{\gamma} = 0 \quad \text{for } \tau^2 \leq \tau_0^2 \quad (11)$$

- (3) Hamersma *et al.* (1981) used the properties of analytical exponential function (exp) including its Taylor series owing which the singularity is eliminated. Their model is written in shear stress

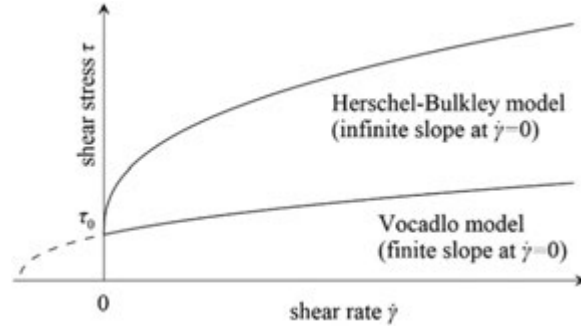


Fig. 2 A comparison of the Vocadlo and Herschel-Bulkley models.

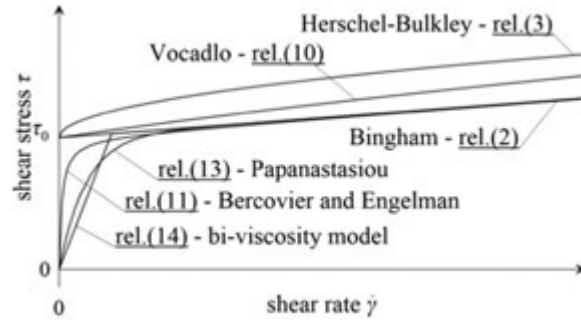


Fig. 3 Comparison of smoothened empirical models.

$$\tau = \left\{ \eta_{\infty} / \left[1 - \frac{\tau_0}{\tau} (1 - e^{-a\tau}) \right] \right\}^{-1} \dot{\gamma}. \quad (12)$$

Later this model was rearranged into the form (Papanastasiou, 1987)

$$\tau = \left[\eta_0 + \tau_0 \frac{1 - \exp(-n|\dot{\gamma}|)}{|\dot{\gamma}|} \right] \dot{\gamma}. \quad (13)$$

- (4) Introducing so called bi-viscosity model Lipscomb and Denn (1984) suppressed the singularity τ_0 at $\dot{\gamma} = 0$ by approximating flow behavior in the vicinity of $\dot{\gamma} = 0$ by a (short) linear segment (Newtonian behavior)

$$\tau = \left[\eta_{\infty} + \frac{\tau_0(1 - \eta_{\infty}/\eta_0)}{|\dot{\gamma}|} \right] \dot{\gamma} \text{ for } \tau^2 \geq \tau_0^2; \quad \tau = \eta_0 \dot{\gamma} \text{ for } \tau^2 \leq \tau_0^2 \quad (14)$$

Approximation of such flow behavior is reciprocal to that of Sisko (1958)

$$\tau = (\eta_{\infty} + K|\dot{\gamma}|^{n-1})\dot{\gamma} \quad (15)$$

who consecutively predicts first power-law and then Newtonian behavior.

Interplay among the above stated smoothened (eliminating singularity) models is depicted in Fig. 3.

Modeling monotonous behavior of a viscosity function based on a combination of the classical models or their generalization

Yasuda *et al.* (1981) incorporated one more parameter into the 4P Carreau model. This new 5P Carreau-Yasuda model is of the form

$$\tau = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{\left(1 + (\lambda|\dot{\gamma}|)^a \right)^{(1-n)/a}} \right] \dot{\gamma}. \quad (16)$$

Chynoweth and Michopoulos (1997) rescaled shear rate $\dot{\gamma}$ in the Cross model and received

$$\tau = \left[\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \exp((\log \dot{\gamma} - a)/d)} \right] \dot{\gamma}, \quad (17)$$

where the parameters in the Cross model are reformulated by the relations $k = \exp(-a)$, $n = 1/d$.

A combination of the Meter and power-law models was presented by Theodoropoulou *et al.* (2001)

$$\tau = \left[K^{1/m} \tau^{1-1/m} + \frac{\eta_0 - K^{1/m} \tau^{1-1/m}}{1 + (\tau/\tau_c)^{n-1}} \right] \dot{\gamma} \quad (18)$$

while the Bingham and Williamson models by Philippov *et al.* (1993)

$$\tau = \tau_0 + \left(\eta_{\infty} + \frac{A}{B + |\dot{\gamma}|} \right) \dot{\gamma}. \quad (19)$$

for a description of viscoplastic materials.

For rheological characterization of the concentrated compounds there are also useful the combinations of the Cross model and the generalized Herschel-Bulkley one (SIGMA Engineering GmbH, 2012)

$$\tau = \left[\frac{\eta_0}{1 + \left(\frac{\eta_0 \dot{\gamma}}{a} \right)^{1-n}} + \tau_0 \cdot \left(\frac{1 - e^{-b\dot{\gamma}}}{\dot{\gamma}} \right) \right] \dot{\gamma} \quad (20)$$

and the 5P CARPOW model combining the Carreau and power-law models (Geiger, 2009)

$$\tau = \left[\frac{a}{\dot{\gamma}^n} + \frac{b}{(1 + c\dot{\gamma})^d} \right] \dot{\gamma}. \quad (21)$$

This model is discussed in more detail in Geiger *et al.* (2019).

The combination of the Bingham and modified Cross models gives (Suri *et al.*, 2004)

$$\tau = \left[\frac{\tau_0}{\dot{\gamma}} + \frac{\eta_0}{1 + (\eta_0 |\dot{\gamma}|/\tau^*)^{1-n}} \right] \dot{\gamma}, \quad \eta_0 = A \cdot \exp\left(\frac{T_{ref}}{T}\right), \quad (22a, b)$$

where τ^* is the transition shear stress and T_{ref} is the reference temperature.

Concentrated compounds behavior can be also described (Hieber and Chiang, 1992) by the modified Cross (23) and Carreau (24) models with introducing the WLF (Williams *et al.*, 1955) model (25) respecting temperature conditions

$$\tau = \left[\frac{\eta_0}{1 + (\eta_0 |\dot{\gamma}|/\tau^*)^m} \right] \dot{\gamma}, \quad (23)$$

$$\tau = \left[\frac{\eta_0}{\left(1 + (\eta_0 |\dot{\gamma}|/\tau^*)^2 \right)^{(1-n)/2}} \right] \dot{\gamma}, \quad (24)$$

with

$$\eta_0 = A \cdot \exp \left[-\frac{B(T - T^*)}{C + (T - T^*)} \right], \quad (25)$$

where τ^* is the critical stress level at the transition to shear thinning and T^* is the glass transition temperature. Hieber and Chiang (1992) showed better efficiency of the Cross-WLF model.

The above stated models as e.g., Cross, Carreau, Carreau-Yasuda exhibit strong symmetry in-between the first Newtonian plateau η_0 and the second one η_{∞} . It means that the drop-off in viscosity from η_0 is mirrored by its rapid levelling-off towards η_{∞} . With the onset of new rheometers providing rheometrical measurements over several orders of magnitude of e.g., shear rate a necessity to describe behavior of materials over the whole measured range revealed “stiffness” of the mirroring. However, in this case “moderateness” of a number of adjustable parameters (up to five) has to be violated. Roberts *et al.* (2001) introduced 8P model, two parameters serving for an intermediate passage between both Newtonian plateaux as in the classical models, but 3 more parameters for a description of either wing. The so called composite Ellis model is expressed in the form

$$\frac{\eta - \eta'_{\infty}}{\eta'_0 - \eta'_{\infty}} = \frac{1}{1 + (\tau/\tau_c)^m} \quad (26)$$

where the “left” and “right” wings are modeled as

$$\eta'_0 = \eta_0 \cdot \left(1 + (\tau/\tau_1)^r \right)^{-1} \quad (26a)$$

$$\eta'_{\infty} = \eta_{\infty} \cdot \left(1 + (\tau/\tau_2)^s\right) \quad (26b)$$

As expected, the classical common number of parameters (3–5) is no longer tenable and with complexity of the studied materials more parameters are required. Nevertheless, it is necessary to have still in mind uniqueness of the individual parameters and their participation. This is also reflected in the following section.

Modeling non-monotonous behavior of a viscosity function

Behavior of viscosity of some new materials is not possible to describe using a monotonous function as both shear thinning and shear thickening (regardless of their order) is present.

For the case of only one change in monotonicity (thinning-thickening or thickening-thinning, in other words an existence of only one global minimum or maximum) David and Filip (2004) introduced the following 6P model

$$\eta = \frac{\eta_0 e^{-f} + \eta_{\infty} e^f}{b + e^{-f} + e^f}, \quad (27)$$

where

$$f \equiv f(\dot{\gamma}; c, p, q) = \text{sign}(\log(c\dot{\gamma})^p) \cdot |\log(c\dot{\gamma})^p|^q. \quad (27a)$$

The non-negative parameters η_0 and η_{∞} determine the initial and terminal Newtonian plateau, respectively. The parameters c , p , q are supposed to be positive. Choice of a parameter b (a requirement $b > -2$ ensuring positiveness of a denominator) determines the course of the viscosity function (under the assumption $\eta_0 > \eta_{\infty}$ for $\eta_0 < \eta_{\infty}$ the sequence of the individual regions is analogous).

- if $-2 < b < 0$, then the proposed model describes sequentially an initial Newtonian plateau, a shear-thickening region, from the point where a viscosity maximum is attained a shear-thinning region, and finally a terminal Newtonian plateau;
- putting $b = 0$ indicates modeling of a pure shear-thinning material;
- for $b > 0$ the sequence is following: an initial Newtonian plateau, a shear-thinning region, from the point where a viscosity minimum is attained a shear-thickening region (in some cases this region is almost negligible), and finally a terminal Newtonian plateau (in the case $\eta_{\infty} = 0$ a shear-thickening region vanishes).

Various forms of viscosity curves are shown in Fig. 4. Applicability of this model (its generalization) in powder injection molding process is demonstrated in Hausnerova et al. (2011a).

In the case of more changes (thickening-thinning-thickening or thinning-thickening-thinning) more adjustable parameters are necessary to apply. Galindo-Rosales et al. (2011a,b) published the 11P model describing consecutively shear thinning, shear thickening, and shear thinning behavior where each monotonous part was described by its corresponding Cross model in such a way that at local extremes the individual Cross models were coupled. The problem with a determination of local extremes was eliminated in the 10P model introduced by David et al. (2013)

$$\eta = \frac{c_1 \dot{\gamma} + c_2 / \dot{\gamma}}{c_3 + (\dot{\gamma} + 1/\dot{\gamma})^{c_4}} + \frac{c_5 \cdot \exp(f)}{c_6 + (\exp(f) + \exp(-f))^{c_7}}, \quad (28)$$

where

$$f = \text{sign}[\log(c_8 \dot{\gamma}^{c_9})] \cdot |\log(c_8 \dot{\gamma}^{c_9})|^{c_{10}}. \quad (28a)$$

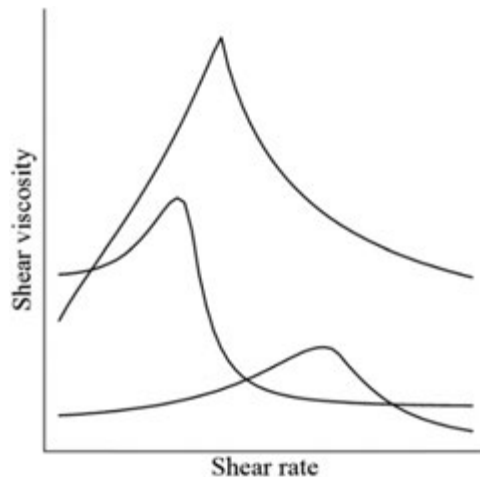


Fig. 4 Variability of 6P model, rel. (27).

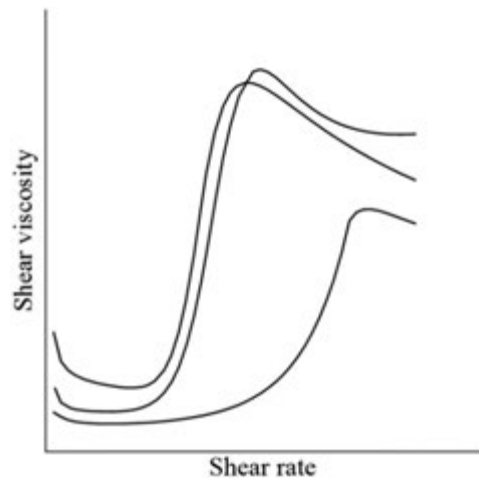


Fig. 5 Variability of the 10P model, rel. (28).

The possibilities of this model are illustrated in **Fig. 5**.

Models With Participation of Material Characteristics

Parallely to the group of constitutive equations introduced above, a series of models describing two-phase flow (solid particles in a carrier liquid) were consecutively proposed starting with the well-known Einstein model (Einstein, 1906) for dilute suspensions (up to 5%)

$$\eta_r = 1 + 2.5\phi, \quad (29)$$

where the relative viscosity $\eta_r = \eta/\eta_c$ relates viscosity of suspension η to viscosity of a carrier liquid η_c .

Einstein derived this relation on the theoretical basis; however, its validation by the experiments is excellent. Most of the relations describing (modeling) suspension flow respected this limit case and as a result their expansion to Taylor series transforms to rel. (29) for small percentage of solid particles. This is the case of e.g., the Roscoe-Brinkman model (Roscoe, 1952; Brinkman, 1952)

$$\eta_r = (1 - 1.35\phi)^{-2.5}, \quad (30)$$

the Eilers model (Eilers (1941))

$$\eta_r = \left(1 + \frac{1.25\phi}{1 - \phi/\phi_m}\right)^2, \quad (31)$$

the Krieger-Dougherty model (Krieger and Dougherty, 1959)

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{2.5\phi_m}. \quad (32)$$

Here ϕ_m represents a maximum powder volume fraction, in other words, ϕ_m is the packing factor at which flow is blocked.

Most of the empirical models, however, are unreliable beyond the original data upon which they were based. A 'universal' model equally efficient for low-concentrated suspension as well as for the high concentrated compounds is practically impossible to propose and the question is whether it is desirable. In practice, quite often, modeling of high-concentrated compound is required and in this case there is no longer a necessity to require a transformation of the applied model onto the Einstein relation. This resulted in the proposal of models not bounded by this assumption. In this sense it is possible to mention for instance the Quemada model (Quemada, 1977)

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \quad (33)$$

or the Janardhana-Reddy *et al.* (2000) model

$$\eta \cdot \phi_b = \eta \cdot (\phi_b)_c + \eta_b \cdot (1 - (\phi_b)_c) \quad (34)$$

where η is the concentrated compound viscosity, ϕ_b is the binder volume fraction, $(\phi_b)_c$ is the critical binder volume concentration, and η_b is the binder viscosity (as introduced $\phi_m = 1 - (\phi_b)_c$).

More models with the corresponding description are introduced for instance in the papers by Honek *et al.* (2005), Lapointe *et al.* (2009), Meyer *et al.* (2016), Gonzalez-Gutierrez *et al.* (2016) and Rueda *et al.* (2017).

The common denominator of these models is an appearance of concentration of solid particles and its maximal contents. Two other factors are not introduced:

- (1) characterization of solid particles (size, shape), most models were derived for the spherical particles (including the Einstein model),
- (2) deeper characterization of a carrier liquid (binder) as only viscosity of a carrier liquid as a whole is hitherto considered.

Models considering particles geometry

Optimization of particles geometry does not concern only their optimal efficiencyFF but is also closely related with the financial costs. This is the reason why the spherical nano- or micro-particles are not frequently applied but are substituted by cheaper irregular ones (Dehghan-Manshadi *et al.*, 2017). This aspect has a crucial impact on modeling concentrated compound behavior as traditionally a spherical shape gives a much better chance to describe (evaluate) flow characteristics. Even determination of such basic factor as maximal (theoretical, random) packing can be in the case of irregular shapes problematic. Spherical particles are generally preferred over irregular shapes for higher packing that allows greater density during the processing and consecutively better quality of surface finish after sintering. Nevertheless, on the other side irregular particles exhibit high-quality retention of molded sample forms after debinding.

The experimental studies discussing application of various particles geometry (Zauner *et al.*, 2006; Loebbecke *et al.*, 2009; Contreras *et al.*, 2010; Sotomayor *et al.*, 2010; Mannschatz *et al.*, 2011; Hausnerova *et al.*, 2017; Kim *et al.*, 2013; Aslam *et al.*, 2016; Gonzalez-Gutierrez *et al.*, 2018; Trad *et al.*, 2019; Singh *et al.*, 2020) or a combination of e.g., nano- and micro-particles (see e.g., German and Bose (1997)) are not exceptional, but the theoretical ones proposing model relations are relatively rare.

In connection with particles influence on concentrated compound behavior the following characteristics are taken into account: particle size, particle size distribution, particle shape, particle densification. For their quantitative description the following parameters are introduced:

- particle size distribution is characterized by D_{10} , D_{50} and D_{90} , corresponding to 10%, 50%, and 90% of particles under the reported particle size,
- particle shape factor $S = 4A/\pi d^2$, where S is the measure of particle irregularity, A and d are the area and the diameter of particle projection in 2D, respectively, other forms are also proposed,
- distribution slope parameter $S_w = 2.56/\log(D_{90}/D_{10})$. Large values of S_w correspond to narrow particle size distribution and small values correspond to broad distribution.

Rheological assessment to modeling concentrated compound behavior cannot be optimized with respect to the molding step only as optimal flowability is contradictory to the sintering step requiring minimal shrinkage. In other words, high concentration is required, only 2%–5% below maximal packing (German and Bose, 1997). This is the reason why also bimodal participation of powder is intensively studied (Oh *et al.*, 2017).

Hidalgo *et al.* (2015) introduced the condensed model combining the modified Cross (with the yield stress term), Arrhenius and Mills models. Moreover, the coefficient preceding these models includes the characteristics of the particles

$$\tau = \frac{D_{60}}{D_{10} \cdot D_{50}} \exp\left(\frac{E_a}{RT}\right) \left(\frac{\tau_0}{\dot{\gamma}} + \frac{\eta_0}{1 + k \cdot \dot{\gamma}^n}\right) \left(\frac{\phi_m}{\phi_m - \phi}\right)^m, \quad (35)$$

where E_a is the activation energy, R is the universal gas constant, T is the temperature. The Arrhenius equation is the most frequently used model for a description of temperature influence in simulation of injection molding.

Claudel *et al.* (2017) introduced the model combination in the following form

$$\tau = \frac{D_{60}}{D_{10} \cdot D_{50}} \exp\left(\frac{E_a}{RT}\right) \cdot \eta_0 \cdot [1 + (\lambda \dot{\gamma})^a]^{\frac{n-1}{a}} \left(1 + \frac{\tau_0}{\dot{\gamma}} + \frac{\eta_0}{1 + k \cdot \dot{\gamma}^n}\right) \left(\frac{\phi_m}{\phi_m - \phi}\right)^{b \cdot \log(\dot{\gamma}) + c}. \quad (36)$$

An analogous model was proposed by Jung *et al.* (2015) combining (multiplying) the power-law model, the Krieger-Dougherty model and the term related to particles description

$$1 + m_1(d^{-1} - d^{*-1}) + m_2(d^{-2} - d^{*-2}), \quad (37)$$

where d is the mean particle diameter, d^* is the reference diameter, and m_1 and m_2 are the constants.

Based on an image analysis of interparticle distances Park and Park (2018) proposed the model of the form

$$\tau = \left[m \exp\left(\frac{E_a}{RT}\right) \dot{\gamma}^{n-1} \left(1 - \frac{\phi}{\phi_m}\right)^{-B \phi_m} \right] \dot{\gamma}, \quad (38)$$

where B is the intrinsic viscosity.

Models respecting binder composition

One of the keen shortcomings of the constitutive equations involving concentration of solid particles is a complete absence of binder composition. In some models binder viscosity has its place as a whole regardless its composition. As mentioned above, quality of final products can be preserved under corresponding packing of a compound, which is – on the other hand – reflected in

a reduction of flowability. To compensate it, various additives are used, very often stearic acid. Its presence in very low concentration (up to 5% in binder composition which implies up to approximately 3% in feedstock composition) has a very positive influence on a feedstock flowability. In spite of its low participation, rheological behavior significantly subjects to its presence (Filip *et al.*, 2019; Hnatkova *et al.*, 2019). To optimize its contents in the individual feedstocks it would require to repeat the whole simulation process just from the very beginning with any negligible change in its concentration.

However, not only changes in additive contents participate in changes of viscosity. Another factor is represented by the changes of a molecular weight of a binder major (backbone) component. As known from chromatographic analysis, the data indicated by the producers are only tentative and differs sometimes non-negligibly within the individual batches. This aspect should be also reflected in modeling real compound viscosity.

One of the efficient solution how to condense all the inputs including Bagley and Weissenberg-Rabinowitsch corrections is a proposal of so called master curves for individual feedstocks. As an example it is possible to refer to the study Filip *et al.* (2020) where an often used nickel-chromium-based compound (Inconel 718, content 59 vol%) with thermoplastic binders of different molecular weight of polyethylene glycol was analyzed. The advantage of true master curves over other models is absence of any adjustable (fitting) parameters. In this case the reported algebraic relations enable to express directly true feedstock viscosities in dependence on PEG (polyethylene glycol) molecular weight and stearic acid concentration. The Bagley and Weissenberg-Rabinowitsch corrections are already included. This approach eliminates the hitherto used non-Newtonian index, by means of which the logarithmic derivative in the Weissenberg-Rabinowitsch correction was approximated. In this case the accuracy of master curves does not exceed experimental errors.

Pressure-Affected Processability of Concentrated Compounds

Although still disregarded in the majority of rheological studies, pressure during injection molding might significantly alter flow properties of highly concentrated compounds. The lack of reliable data even for pure polymer melts arises from ambiguous definitions of pressure sensitivity coefficients, various evaluation techniques and test artefacts connected.

Pressure is mostly accounted for via well-known exponential relation between viscosity and pressure proposed by Barus (1893)

$$\eta_0(P, T) = \eta_0(T)e^{\beta P} \quad (39)$$

where η_0 is the viscosity at zero shear rate, P and T stand for the pressure and temperature, respectively, and β represents the pressure coefficient.

If, simultaneously, an influence of temperature and pressure is taken into account – modified WLF equation introduced by Tschoegl *et al.* (2002) is usually employed. Nowadays, commercially available softwares allow implementing alternative models, e.g., the standard Cross-WLF model with the optional dependence on pressure. Costa *et al.* (2015) have shown the large deviation of the simulations with and without intercepting the pressure dependency of viscosity. They also demonstrated that the Barus model and standard (Autodesk®) pressure dependence model resulted in the similar result during the filling phase when melt temperatures do not change significantly. On the opposite, if a simple exponential form of the pressure dependence is substituted with a quadratic exponent as suggested by Goubert *et al.* (2001), the predicted pressure trace of a cavity pressure shows an incorrect trend, and thus no improvement.

Evaluation of Pressure-Dependent Viscosity

In order to evaluate viscosity's sensitivity to pressure, direct (experimental) or indirect (analysis and/or correlation to other properties, e.g., free volume) approaches can be concerned.

Indirect evaluation of pressure-dependent viscosity is based mainly on the calculations from Bagley plots intercepting non-linearities in the pressure profiles (Duvdevani and Klein, 1967; Penwell and Porter, 1969, 1971; Kamal and Nyun, 1973, 1980; Denn, 1981; Laun, 1983; Izu *et al.*, 1993; Hatzikiriakos and Dealy, 1994; Moldenaers *et al.*, 1996; Hay *et al.*, 1999; Liang, 2001a,b). Utracki (1983, 1985) put an enormous effort to derive pressure-affected viscosity from PVT data with the help of Simha-Somcynsky equation of state as an alternative indirect technique. Decades later, Sedlacek *et al.* (2005) successfully substituted Utracki's empirical constants, which had to be set for each individual material with a unique coefficient correcting reduced compressibility.

However, if Utracki's method and calculations from Bagley plots were compared to a direct measurement of pressure-dependent viscosity on a modified rheometer, the better reliability of a direct measurement was reported (Goubert *et al.*, 2001). Another advantage is that modified rheometers are able to cover various flow situations occurring during high-pressure processing as injection molding. Single piston equipment, used by Choi (1968), Driscoll and Bogue (1990), Baker and Thomas (1993), Thomas (1997), Binding *et al.* (1998, 1999), Couch and Binding (2000), Carter (2000), Goubert *et al.* (2001), and Sedlacek *et al.* (2005) is modified with a secondary chamber with a restricting needle generating backpressure as schematically shown in Fig. 6.

Double piston rheometers generate the pressure in the system closed between the two pistons as shown by Maxwell and Jung (1957), Westover (1961, 1966, 1991), Carley (1961), Ito *et al.* (1972), Lord (1979), Kadijk and Van Den Brule (1994), and Mackley and Spitteler (1996). Equipment based on a drag flow as Couette viscometers or sliding plate rheometers were adopted into pressurized versions by Semjonow (1962, 1965, 1967), Cogswell and McGowan (1972), Cogswell (1973), Koran and Dealy (1999). Also, some of the online

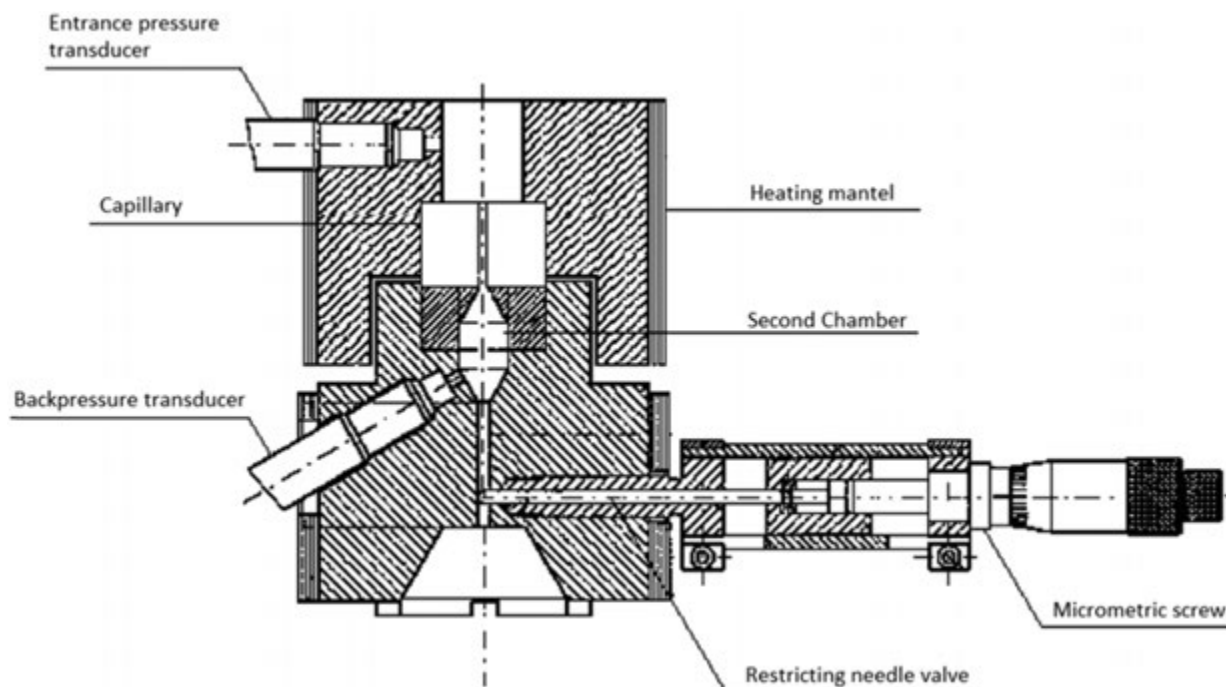


Fig. 6 Modified single capillary rheometer (according to Sedlacek, T., Cermak, R., Hausnerova, B., *et al.*, 2005. On PVT and rheological measurements of polymer melts: correction of the hole fraction-viscosity relationship. *International Polymer Processing* 20, 286–295).

rheometers were recently adapted for pressure effect measurements; e.g., [Friesenbichler *et al.* \(2011\)](#) proposed the injection molding machine-based rheometer achieving shear rates up to 10^6 s^{-1} with the servo-hydraulically regulated piston to measure a pressure dependence of viscosity.

Pressure-Dependent Viscosity of Highly Concentrated Compounds

Currently, the modification of the rheometers to allow a measurement of pressure dependent viscosity has been fully commercialized, but there is still very limited number of papers devoted to highly concentrated compounds.

[German \(1995\)](#) only assumed that sensitivity of viscosity to pressure will be reduced due to a presence of powder. This trend was experimentally confirmed by [Hausnerova *et al.* \(2006\)](#) for cemented carbides only for low to moderate (up to 30 vol%) powder concentrations. At higher concentrations (50 vol%) the pressure sensitivity was enhanced in comparison to pure polymer binder ([Hausnerova *et al.*, 2009](#)) suggesting that at low to moderate loading levels the pressure sensitivity of the compounds is governed by the sensitivity of the polymer binder component, which is connected to the free volume changes following their structure, whether at high powder concentration the driving factor is the compressibility of powder structures formed within binder and their reorganization during pressurization. In this respect, a strong effect of the particle size distribution, and especially portion of small particles, on pressure dependent flow behavior was reported ([Hausnerova *et al.*, 2011b](#)) with the important finding that the pressure sensitivity of the highly concentrated compounds can be altered by modifying powder characteristics.

Based on a number of papers starting with the pioneer work of [Vinogradov and Ivanova \(1967\)](#) it should be pointed out that the pressure is also the reason of non-linearities and/or negative intercepts of Mooney plots discussed above. In this respect, [Mazzanti and Mollica \(2017\)](#) proposed a pressure dependent wall slip constitutive model supported by the experiments on a wood polymer composite. The model has seven parameters, including a yield stress, and fits the experimental data much better than the power law model.

Pressure-Volume-Temperature Data to Process Optimization

The pressure factor is also accounted for in pressure-volume-temperature (PVT) diagrams, which represent a fundamental thermodynamic characteristic necessary for computer simulations of the processing by injection molding, where inhomogeneous shrinkage, warpage and sink marks are related to the specific volume changes governed by pressure and temperature.

Simulation of shrinkage and warpage is related to cooling of molded materials to a solid state, which is not equilibrium state, and therefore, empirical models are employed to fit the PVT data rather than the theoretical ones. Also, one of the main general drawbacks still remaining is that cooling during processing is performed at higher rates than PVT measurement apparatuses allow ([Pantani and Titomanlio, 2001](#)).

Mostly, the PVT data are implemented to the simulation tools with the help of the two-domain Tait model which is of the form

$$v(T, p) = v_0(T) \left[1 - C \ln \left(1 + \frac{p}{B(T)} \right) \right] + v_t, \quad (40)$$

$$v_0(T) = b_1 + b_2 * T, \quad (40a)$$

where v is the specific volume of the material, v_0 is its reference specific volume, T is the temperature, p stands for the pressure, C is the constant 0.0894, B represents the pressure sensitivity coefficient, and b_1 and b_2 are the fitting parameters.

The two-domain Tait model has a higher accuracy than other employed empirical models as rather simple Spencer-Gilmore model (Spencer and Gilmore, 1950), or the two-domain Schmidt model having 13 coefficients (Schmidt, 1986). It consists of two independent sets of equations, because the solid phase and the molten phase are described separately. The specific volume at the transition state between melt and solid is not continuous, which makes the calculation of the specific volume inaccurate and leads to an unstable prediction in the simulation of injection molding. These issues were quite recently addressed by Wang *et al.* (2019a), who developed the continuous two-domain Tait model, which however has not been utilized for highly concentrated compounds yet.

As already stated above, highly concentrated compounds are usually admixed to multicomponent binders with different transition temperatures, and therefore have more than one transition region. Thus, the relevance of currently available empirical models such as the Tait model in simulations of highly concentrated compounds is even more disputable (Heldele *et al.*, 2006), although often employed – recently e.g., by Lin *et al.* (2018) to optimize processing conditions of Ti-6Al-4V parts exhibiting excellent physical and mechanical properties showing the final density of 99.8%. Walale *et al.* (2018) studied the ceramic powder (mixture of alumina and fused silica) admixed into a wax binder and treatment of the PVT data with the modified Tait model was proved effective in studying/simulating interactions among temperature, pressure and holding time with respect to shrinkage directions.

PVT data serve as an important source of the information concerning volume (and correspondingly shrinkage) changes induced by pressure and temperature simultaneously. Greene and Heaney (2007) clearly showed the direct correlation between the green shrinkage (after molding) and shrinkage calculated from PVT data, and confirmed the usefulness of PVT data for enhancing the accuracy of the predictions of the overall shrinkage. On a carbonyl iron filled (61.1 vol%) in a wax/polymer binder they also proved that the calculated shrinkage and hold pressure could be used to effectively control dimensions of the final sintered components.

As another example, Boehme *et al.* (2009) measured coefficient of thermal expansion and curing shrinkage for two (vitreous silica and carbon black) highly-filled (82 – 94 wt%) resins. Crosslinking kinetic was evaluated using the DSC and PVT methods. The experimental data of curing shrinkage during crosslinking, quantified via decrease of specific volume, was precisely fitted with the Tait model. At this point, it should be stressed again that there is a significant difference between the values of the parameters (heating and cooling rates) in the process and in the research performed with DSC and determining PVT data (Kutsbakh *et al.*, 2019). Following the study of Wang *et al.* (2019b), who showed that for semicrystalline polymers the specific volume increases with increasing cooling rates in the crystallization and solid state, and decreases with increasing heating rates in the crystallization and molten state, and that it also decreases with increasing compression rates but decreases then increases with increasing decompression rates, this aspect should be (and currently is not) considered with caution in flow simulations of highly concentrated compounds, because semicrystalline polymers as polypropylene or high/low density polyethylenes are frequently employed as the binders for these materials.

As already pointed out, PVT data acquisition is affected by the measurement technique. Two different PVT measuring modes can be performed: isobaric to determine the thermal expansion coefficient and isothermal to determine the compression coefficient. Suárez *et al.* (2015) analyzed the existing PVT testing methods and devices with the conclusion that they still have shortcomings regarding cooling, shear rate and compression speed, and especially the pressure distribution and compression speed should be taken into account.

First, there is the confining-fluid technique as with high-pressure mercury dilatometer (Gnomix, USA) developed by Zoller *et al.* (1976) and later proposed also by Zuidema *et al.* (2001) and Tardif *et al.* (2013), where the material tested is under hydrostatic pressure at all states (solid, molten, and re-solidified). Laddha *et al.* (2009) used Gnomix for the study of an alumina powder (56 vol%) filled in an in-house and commercial feedstocks to understand the compression and temperature effects during injection molding. The PVT data in the range of pressure from 0 to 500 MPa up to 200°C were fitted with the Tait model.

With the same apparatus, the effect of powder concentration on glass transition temperature obtained from PVT data was considered by Chandra *et al.* (2010) for 20 and 40 vol% lead titanate in PMMA matrix. Transition temperature was shifted to higher values as powder content decreased, and thermal expansion coefficient changed also, enhanced at pressure up to 200 MPa.

Another study taking into account the effect of powder concentration, and also particle size distribution of highly filled (50 vol%) cemented carbide compounds on their pressure-volume-temperature characteristics and thermal properties was performed on a Gnomix (Hausnerova *et al.*, 2013) revealing that the pressure influences both detected phase transitions, but only for higher transition it causes a different effect on the melting and crystallization of the material. The discrepancies in specific volumes at applied pressure diminished with increasing powder content, whereas melting temperatures remained unaffected. Volumetric thermal expansion coefficient and compressibility were linearly and exponentially, respectively, dependent on pressure. The variance

in the particle size distributions of carbide compounds resulted in shifts in both volumetric thermal expansion coefficients and compressibility values.

PVT data obtained with the Gnomix apparatus were also employed in mold-filling simulations to understand the effects of powder content on the process parameters and defect evolution during the injection-molding process for highly concentrated compounds of barium titanate (Onbattuvelli *et al.*, 2011), aluminum nitride (Kate *et al.*, 2012), silicon nitride (Lenz *et al.*, 2012), mullite-zirconia (Martin *et al.*, 2013), Ni-based superalloy powder (Lee *et al.*, 2020).

However, the piston-die techniques as PVT-100 (SWO Polymertechnik, Germany) are more frequently used to derive PVT data. In 2004, the PVT testing procedure was standardized in ISO 17744 (International Organization for Standardization, 2004) for piston operated instruments. The main disadvantage of this approach lies in applying non-hydrostatic pressure, but with PVT-100, there are also other issues connected as that the tested molten materials adhere to the die and/or leak between piston and die during measurements. PVT-100 was modified by Hobbs and Brown (1999) to intercept range of testing conditions (both cooling rate and pressure) closer to injection molding, but it failed in terms of cooling rate parameter. Bearing the same attempt in mind, Forstner *et al.* (2009) designed the apparatus capable to measure at the conditions closer to real processing via injection molding.

Persson *et al.* (2009) studied the thermal properties of 60 vol% metal (420 stainless steel) based compounds using the PVT-100 device. Regardless of powder concentration, the transition zones corresponding to the particular organic components of a binder derived from the PVT data revealed the melting temperature shift from 62 to 66°C as pressure varied from 150 to 350 MPa. Wei *et al.* (2000) investigated the pressure influence during injection molding process using the same tool (PVT-100) for 85 wt% alumina in a paraffin wax based binder at pressures from 0.1 to 120 MPa with the similar results. Hausnerova *et al.* (2011a) also optimized powder injection molding of feedstock based on aluminum oxide and multicomponent water soluble polymer binder with help of PVT data obtained from the PVT-100.

Fu *et al.* (2006) employed PVT data obtained with the PVT-100 to analyze the sources of demolding failure of micro metal injection molded parts. They found out that both shear stress during ejection and thermally-induced stress during cooling of metal micro-parts are the reason for the unresistful demolding, and they can be to some extent compensated by optimizing demolding temperature and holding pressure.

Currently, capillary rheometers (Göttfert, Germany) are adopted for the measurement of PVT data most recently by Wang *et al.* (2019b). The temperature ranges from a maximum processing-allowed temperature (usually below 200°C) sweeping down to about 30°C to cover the entire processing and cooling window of the materials. At each temperature level, the rheometer applies a force according to the investigated pressure level, and the contraction of the sample with temperature is measured. Rodriguez *et al.* (2016) evaluated the pressure coefficients for nanocomposites with the help of pressure-volume-temperature data from the PVT-100, and the pressure coefficients at constant shear rate and constant shear stress measured in a pressure chamber of a capillary rheometer Göttfert Rheograph 25. Their results coincide well with those obtained by Pantani and Sorrentino (2005) for a pure binder employed (polystyrene). As expected, the PVT results revealed the most significant differences between the unfilled and filled samples reflecting the variation of the glass transition with pressure, while rather surprisingly, pressure coefficients at constant shear stress remained unaffected by fillers.

Besides confining fluid and piston-die approaches, there have been done some attempts to employ injection molds and machines directly (Wang *et al.*, 2010) or universal testing machine by installation of two pistons pressing material located between them (Rudolph *et al.*, 2011). Very recently, Muranov *et al.* (2020) derived PVT parameters from an in-house plunger dilatometer, and with the help of DSC showed that the phase transition temperatures of polypropylene and wax used as binder components for MIM-410 stainless steel compound raised up considerably with a pressure increase of 100 MPa. They proposed a technological window of parameters that allow for injection molding of highly concentrated compounds with minimal volume shrinkage.

Unfortunately, in some relevant studies (e.g., Binet *et al.* (2005), Greene and Heaney (2007)), the description of the evaluation procedure is not presented.

Concluding Remarks

In this article, the overall state of art of some relevant aspects of the investigation of processability of highly concentrated metal and ceramic compounds is presented.

With no doubt, the reliable rheological data is an inevitable input in the simulation procedures. Thus, a catalog containing such data for broad range of material combinations would be of great use in identifying optimized processing parameters without the requirement of expensive empirical trials. However, as stated by Kate *et al.* (2017): "Whereas injection-molding simulation platforms typically offer over 5000 listings of property datasets for polymers, there are presently fewer than 5 such listings for ceramics and metals".

Although the issues limiting the relevance of the current findings were addressed through the previous sections, there might be always found some arguments mitigating rather critical conclusions. As an example, even if the PVT data currently evaluated are still not as reliable as they should, they are employed successfully to simulate the effects of injection molding parameters such as holding time, packing pressure and melt temperature on shrinkage and warpage of molded parts made of highly concentrated parts as recently shown by Walale *et al.* (2018). They quantified and simulate dimensional deviations due to shrinkage and warpage of ceramic parts of quality-highly-demanding application for gas turbines in aerospace.

One might also argue that the PVT data of high concentrated compounds are largely governed by employed polymer binders, which represent only a temporary vehicle enabling the processing of metals and ceramics by injection molding. Hence, their importance for optimization of the final metal and ceramic parts performance, might be disputable. As an example, Krug *et al.* (2001) provided a thorough study of the relationship between the cracks obtained with ceramic compound and the morphology resulting from the melting/cooling during/after injection molding. As a case material they selected commercially available alumina/polyoxymethylene feedstock. Molded parts showed a grainy fracture surface, where crack paths followed the boundary of binder spherulites, which size was found to depend on a cooling rate, and hence on position in the molding. But, after debinding and sintering, the final ceramic parts revealed smooth surfaces. In the fundamental science, however, the researchers should be aware of limits and hindrances, the evaluation of the pressure effect on the processing performance of highly concentrated compounds exhibits.

Regardless of the long-term fundamental existing knowledge, the rheological models currently employed in the studies of high concentration compounds are those unable to intercept the complexity of their flow performance. Efficient simulation of the operational units processing concentrated compounds is significantly based on rheological modeling. Due to complexity of the whole problem it is not possible to expect a replacement of frequently used empirical and phenomenological models by their physically based counterparts. Comprehensive characterization using powder concentration and maximal packing is an integral part of many models describing shear viscosity. However, with the onset of nanomaterials and a combination of nano- and micro-particles an emphasis should be more intensively paid to their participation in the individual steps not only qualitatively but also quantitatively in the form of introducing powder characteristics into the constitutive models. The analogous approach seems to be beneficial in more detailed description of a binder taking into account its individual components as seemingly almost negligible change in binder composition can evoke non-marginal changes in rheological behavior. With respect to geometrical arrangement of the molding step a detailed study of elongation viscosity should be also intensively analyzed. Nevertheless, for sound application of every model the data should be a priori processed using Bagley and Weissenberg-Rabinowitsch corrections thus ensuring a passage from apparent to real behavior.

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Composites for Sensors and Actuators

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Introduction

Composites have the advantage of combining significantly different types of material. It integrates reinforcing materials to feature functionalities like load bearing capacity, superior mechanical and tribological properties, wear and corrosion resistance, sensing and/or actuation. Composites having sensing and actuation properties are known as adaptive materials or intelligent materials. These materials are integrated with sensors and actuators that are connected through a controller. These adaptive materials can identify the material conditions in service (like pressure, temperature, shape, loads, damage, etc.). Also, the intelligent materials may be capable of adaptive actuation (like inner stresses, color, temperature, stiffness, shape, changing deformation, etc.). The controllers linking the sensor and actuator may be incorporated into the composite itself, but in majority of the cases, it is outside the material. Polymer resin is mainly considered as the matrix material for such composites, however, concrete or metal matrices have also been considered.

Control Options, Sensors and Actuators

Control Options

Numerous sensors and actuators are to be controlled in the composite structures. A feedback and feed forward control options are the classical procedures for the composites. For novelty detection and pattern recognition, importance of artificial neural networks (ANN) has been understood. For advanced sensor signal processing and automatic attainment of optimal solutions, wavelet transforms and genetic algorithm procedures have been used respectively.

Sensor Options

Any classical structural constituents previously prevailing in a composite may be employed as sensors. For instance, differences in the electrical resistance of carbon fibers can be utilized for examining damage like fiber or matrix break down, delamination etc. Other applications include optical fiber sensors that are united with usual structural composites. Polyamide-clad Bragg grating sensors are one of the common types of such composites. Piezoelectric materials available in both polymers and ceramics may also be used as another option. These piezoelectric materials when exposed to stress, emits a voltage and can be molded to any form and size and integrated into or adjusted onto the composite. Besides, when a voltage is applied, these piezoelectric elements can also function as actuators.

Actuator Selections

Generally ceramics, i.e., piezoelectric materials, are used as actuators due to their very rapid response and high precision (example, PZT, lead-zirconate-titanate). However, these piezoelectric actuators are suitable for dynamic loading conditions. Fibers or patches can be bonded onto or integrated into the composites (Hohlfeld *et al.*, 2019). Very small relative deflections may be achieved which influences the damping actions of structures (Hairong *et al.*, 2018). Leverage mechanisms need to be used for achieving larger deflections. In these applications, the low allowable strain manifested due to the brittleness of the piezoelectric ceramics must be considered. For actuators, magnetostrictive materials possess almost or slightly comparable to piezoelectric materials. Magnetostrictive materials consist of a magnetic field instead of an electric field.

Ionic polymer metal composites (IPMCs) are types of polymeric composites worth mentioning. Depending on charged polyelectrolyte membranes, for instance, poly (acrylic acid) (PAA), poly (vinyl chloride) (PVC) and collagen or fibrous protein, these are mostly used as artificial muscles. While applying low voltage (4–7 V), IPMCs shows large deformation (> 10%) and operates best in a humid environment. But in dry environments, these IPMCs can be made to act as self-contained encapsulated actuators (Ansaf *et al.*, 2018). The densities of these IPMCs are similar to the above-mentioned polymers; however, the reaction time is of the order of a microsecond to a second, and thus these are faster. The damping characteristics of materials are greatly influenced by the application of electro rheological fluids (ERF). These consist of polarizable particles (example, cornstarch), water as an activator and a dielectric liquid (example, oil). Their rheological properties (example, viscosity) are changed due to the use of an electric field. In absence of electric field, these particles are unevenly distributed. But, in presence of an electric field, these particles are arranged systematically according to the field lines, heading to more rigid behavior of the fluid.

Materials and Design Considerations

The compatibility between the host material and the sensing/actuation is one of the major considerations for designing composites meant for sensors and actuators. One of the significant parameter is the stiffness ratio between these constituent materials. The sensing or actuation material must not be too soft, as the transfer of actuation will be difficult to the host material or else the sensing material for the sensing design. For good design, the stiffness ratio should lie between 0.5 and 2 and the quality of interface between the constituting materials should be good. These materials must be capable of transferring substantial amount of shear stresses. Or else, the actuating materials will function as artificial delamination. Any form of chemical incompatibility, or generation of high temperature due to heating of actuation element may result in poor interface stress transfer between the materials.

When these sensing/actuation materials are being integrated into the composites, the quantity, shape and size of these constituent materials is essential to be considered regarding any notch effects these materials may produce during integration (Warkentin and Crawley, 1991). It is beneficial to use numerous small elements widely dispersed in comparison to one bulky element placed at one location only based on the applications (Kaïke *et al.*, 2018). The number and location of actuator elements relies on the function and geometry of the element and the structure considered. Considerations of global component design play a vital role in optimum design of these composite materials. The vast majority of these composites are still at a developing phase. Though, real-world applications of these composites has achieved in generating significant interest in the scientific community.

Fiber Optics

The composites for sensors and actuators generally consist of optical fibers as sensing elements. These fibers generate reliable sensor signal output when embedded in the composites preferably. However, attempts are made to attach the fibers on the surface without hampering sensor's output quality. The diameters of the fibers being $\leq 125 \mu\text{m}$ are considered ideal. The smaller diameter fibers are better for integration into the composites. Larger diameter fibers are formed due to the development of resin rich zones around the fibers. Very thin fibers lead to positioning problems due to electrostatic forces during processing. For significant improvement of the adhesion of the fibers, it is recommended to clean the optical fibers with acetone. The optical fibers are advantageously used as sensors as it does not compromise the structural integrity of the composite. This is because the volume fraction of the fibers required is small compared to the volume fraction of the reinforcing fibers. In addition, the optical fibers are immune to electromagnetic interference and have very low volume and weight. The nodes where the optical fiber emanates out of from the material, the connections and terminations of the fiber optic are some of the critical locations where fracture takes place. Hence, to remove fractures, synthetic rubber implants are placed across the fibers at these nodes (Green *et al.*, 2000).

Piezoelectric Materials

The size of a piezoelectric sensor is few millimeters in diameter and less than 1 mm thick. These piezo ceramic elements can either be bonded onto its surface or integrated into the prepared composite without compromising the strength of the material. Elements of moderately large size as $15 \text{ mm} \times 5 \text{ mm} \times 0.1 \text{ mm}$ are usually required for using piezoelectric elements as actuators. The actuation devices are integrated by preparing special cutouts in the material. To avoid any detrimental effects to the composites, considerable care has to be taken in selecting the appropriate bonding technique. A compressive pre-stress helps to improve the performance of these piezoelectric elements. The actuators at higher frequencies or actuator clusters generated a large amount of heat. Exclusive care needs to be taken during integrating these piezoelectric materials to reduce the effect of heat. The problem of excessive heating can be minimized by applying a special conductive layer for heat transfer. Piezoelectric fibers can be combined like conventional fibers. It prevents any cutouts in the prepared composites. The production of the required electric field can be developed by interdigitated electrode pattern on top and bottom layer of the piezoelectric fibers. This kind of prepared elements can be incorporated in the assembling sequence during actual composite fabrication (Ribeiro *et al.*, 2018).

Other piezoelectric materials for actuators are 1–3 piezoelectric actuator composites. In these composites, the piezoelectric rods are enveloped by a soft matrix. These rods are placed perpendicular to the direction of polarization and are produced by an injection molding process. The sensing and actuation capability of the piezoelectric materials are best exposed when the deformations are required in the thickness direction of a plate. Piezoelectric rubbers and paints have been developed to remove the disadvantage of high brittleness in piezoelectric ceramics. These elements are made on the basis of the principle of a piezoelectric material by milling into a very fine particulate sized powder, mixed to rubber or epoxy resin, and then polarized again to obtain the piezo-electric effect. However, these elements possess reduced sensing and actuation effect in comparison to the initial piezoelectric material.

Electrorheological (ER) Fluids

The cavities between the rubber seals and the composite plates along the thickness axis can be sealed using ER fluids. CFRP plates can be used directly as electrodes and are advantageous because of their electrical conductivity.

Ionic Polymer Metal Composites

The ionic polymer metal composites (IPMC) have countless applications for example low drive voltage (less than 3 V), large displacement, relatively fast response (100 Hz), capability of activation in wet condition or in water, soft material, durability, can be worked in dry condition, can be scaled down at ease (Fujiwara *et al.*, 2000; Onishi *et al.*, 2001). Several IPMC researchers use the Nafion based IPMC actuators as it can be easily produced and can be joined together with sensors and control units to fabricate soft intelligent systems (Asaka and Oguro, 2009). The Nafion can be easily given the required shape by casting the melt away Nafion solutions and evaporating the solvent. Or else, it can be produced by hot molding the thermoplastic type pre-Nafion resin and fabricating Nafion by hydrolysis. In recent times, different metals or metal oxides are chemically plated and conductive nano particles in dispersed solutions, e.g., metal oxide or carbons, are directly coated. The next fabrication step of the IPMC devices that have multiple degrees of freedom is to design the plating electrode. The methods used to pattern the electrodes in the IPMC are based on laser processing, masking and electroplating. Finally, the IPMC actuator is integrated with control and sensor units to fabricate soft and smart systems. The outcome of the IPMC actuator can be regulated by the feedback of the same IPMC sensor signal (Shahinpoor *et al.*, 1998).

Manufacturing Methods

The manufacturing procedure necessary for embedding active constituents within the load carrying configurations is still having a prominent application. There are certain advantages of having both the sensors and actuators implanted into the structures, rather than attaching it to the outer skin (Tuloup *et al.*, 2019). Once inside the host structure, the actuation system is protected from all exterior atmospheric agents that could reduce its performance. Special attention is required to manufacture composites for sensors and actuators as the wiring, sensors and actuators must be defect free that may arise due to chemical, mechanical or thermal reactions during fabrication (Guo *et al.*, 2019). This relates to their location within the composites and their properties. Suitable care may be attained through individual hand laying and bonding that is on the other hand the most expensive process. Early research interests include the integration of active fibers e.g., the piezoelectric materials using mechanized methods. There can be viable alternatives like automated fiber and tape laying if these techniques can be adapted to these new composites. Tape laying/filament winding can be a technique that uses laser energy heating to produce a composite structure layer by layer. However, if the materials are homogeneous, coating technique can be suitably used. The extrusion processes for designing polymer materials such as optical fibers or films of piezoelectric materials can be one of the other cheap manufacturing processes (Fleischer *et al.*, 2018).

Hand Laying and Bonding

The hand lay-up and bonding is one of the oldest open molding techniques of woven composite manufacturing. The hand lay-up process basically consist of four steps, viz., mold preparation, gel coating, lay-up and curing. Curing helps in hardening of the fiber reinforced resin composite without using any external source of heat (Ren, 2008). Initially, the dry fibers in different forms such as knitted, woven, bond fabrics or stitched are manually placed in the mold. The sticking of the material on the mold surface is prevented by using anti-adhesive agent. The top and bottom of the mold plate is covered with a thin plastic sheet to get a smooth surface of the product. The woven reinforcement layers are positioned on the surface of the mold by cutting them in requisite shapes. The resin mixture including all other ingredients is applied onto the surface of the reinforcements in the mold and spread uniformly using a brush. Then, with the help of hand rollers, the interaction between the reinforcement and the matrix of the wet composites are enhanced and the resin is uniformly distribution to get the necessary thickness. After that, the excess polymer and trapped air bubbles are removed by pressing and putting other mat layers on top using a roller. Finally, the laminates are left to cure under standard atmospheric conditions. The product surface quality is enhanced by applying a pigmented gel coat to the mold surface. It requires highly skilled hands to overlay the matrix and the reinforcement that involves resin mixing, laminate the resin contents and quality of the laminate are crucial. It is a slow process and depends very much upon the skill of the workforce. However, this technique is often employed for large and complex parts, when a good surface finish is required on one side only.

Automated Fiber and Tape Laying

Automated fiber placement (AFP) and automated tape laying (ATL) are emerging as one of the advanced methods towards fabrication of polymer based composite structures. Among the various composite processing systems, the use of prepreg tapes is a well-established technique to produce composite components. These techniques offer an elevated level of customization through the possibility of placing individual reinforcement at custom designated trajectories. Automated fiber and tape laying are the processes that use computer guided robotics to lay one or several layers of reinforcing fiber tape or tows onto a mold to create a part or structure (Perner *et al.*, 2016).

Filament Winding

This manufacturing technique can withstand high degree of fiber loading that gives high tensile strength to hollow and cylindrical products such as fuel and chemical storage tanks, stacks, pipes, rocket motor cases and pressure vessels. A high strength to weight

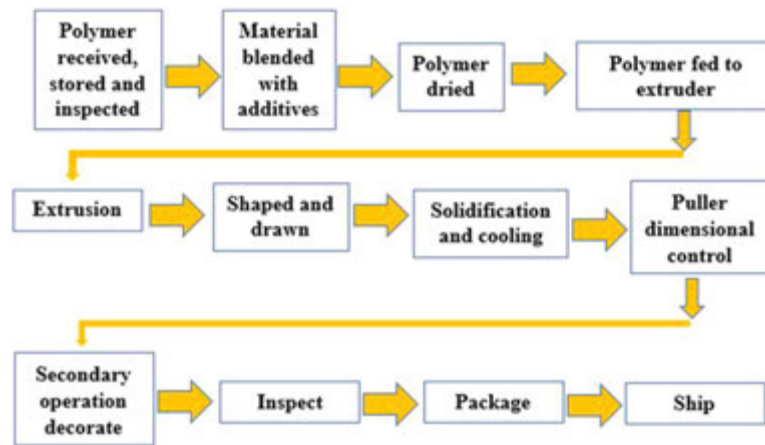


Fig. 1 The Extrusion process.

ratio laminates can be produced that gives a high degree of control over uniformity and fiber orientation. Fiber tows are wound onto a mandrel in different orientations after being passed through a resin bath that is controlled by the fiber feeding mechanism and rate of rotation of the mandrel. Continuous strand roving is fed through a resin bath and wound onto a rotating mandrel. The roving feed runs on a trolley that travels the length of the mandrel. The filament is placed in a predesigned geometric pattern to offer maximum strength in a particular direction. The laminates are then cured on the mandrel after applying sufficient layers. Finally, the molded part is taken away from the mandrel. It uses mandrels of desired shape and size that are made of steel or aluminum to form the inner surface of the hollow part. Moreover, collapsible mandrels are available that helps in part removal. The filament winding process can be used to make structures that are highly engineered and meet strict tolerances. Because filament winding is computer controlled and automated, the labor factor for filament winding is lower than other open molding processes (Gibson, 2010).

Extrusion Procedure

There are two types of extrusion process: the hot processes applied for manufacturing semi-products and the cold processes for the extrusion of components. Furthermore, the extrusion processes are categorized according to the material flow in the direction of the tool movement (radial, backward, forward) and according to the initial shape of the component (solid, hollow). The extrusion is more common in the manufacture of polymer matrix composites. The polymeric material is received, inspected and stored. Before extrusion, the polymer may be blended with additives (oxidative stability, stability for heat, ultraviolet stability, etc.), color pigments or concentrates, flame retardants, fillers, lubricants, reinforcements, etc., to produce the preferred product property profile. In order to remove polymer degradation due to moisture, some resin systems must be dried before extrusion. Some other resins may require drying if they are stored in a cold and warm environment that condenses the moisture on the surface of the flake, pellets, or powder. After drying and mixing of the polymers, it is supplied into the extruder, where it is melted, mixed and delivered to the die to shape the extrude. On leaving the die, the product is cooled and solidified in the preferred shape and drawn away from the extruder at a constant velocity to attain the appropriate cross-section. Consequent operations, i.e., printing, flame treatment, annealing, cutting etc., can be done in parallel after the puller. Finally, the finished product is examined, packed and transported. The complete extrusion procedure is shown in Fig. 1.

Applications

One configuration may be demarcated “intelligent” if it is capable to monitor the functional environment, to collect and expound information and then respond appropriately. In order to achieve these, the structure must be fitted out with a set of sensors, an intricate data acquisition system and an actuation system. Sensors are typically useful for providing system state impressions by observing the responses of the structures. The types of responses normally investigated include thermal gradients acting on structures, chemical analysis for corrosion/erosion and responses due to mechanical loads, strains, vibrations, etc.

Sensing Applications

The determination of structural life of components by monitoring loads is a big challenge. Piezoelectric elements and fiber optics are mainly the sensing elements considered for the purpose. Piezoelectric elements are more commonly used for detecting vibrational loads having frequencies > 10 Hz. Damage monitoring of composite structure components is also a related issue. It includes detection of matrix fracture, identification of delamination of localized fiber due to overloads or impacts (Lou *et al.*, 2019).

For monitoring damage induced loads, optical fibers are mostly used while piezoelectric elements acts as actuators that sends a selected signal into the material which is recorded by another sensor. Thus, non-destructive testing of composite materials becomes an essential element of composite characterization. Carbon fiber reinforced composites are used specifically for observing electrical resistance of composites. It can be done by contacting the carbon fibers with an acceptable current sensing and generating device across the composite. During composite processing, for monitoring the curing process, piezoelectric sensors and fiber optics are well suited. Electromagnetic sensing for radars in general defense and aerospace applications is becoming increasingly popular (Duan *et al.*, 2019). A specially designed composites for electromagnetic sensing popular with ground traffic control is gradually attracting many researchers and scientists.

Actuation Applications

The conception of actuation is related to the ability of measured energy absorption or release. The actuation of the structure should aid to reduce unfamiliar load condition effects thus to reduce fatigue phenomenon and compensating heavy local conditions. There are applications of actuations in the field of medicine, viz., stents or valves, and for vibration damping applications (Li *et al.*, 2008). The active dampening can be used in other functions by means of piezoelectric elements and/or ER fluids. Ample effort is concentrated on active constrained layer dampening using sandwiched structures consisting of the parent structure, a viscoelastic layer, a constraining layer and a PZT actuator. It helps the actuator in distributing its damping energy across the constrained layer over a wider area in an efficient way. Some particular applications include turbo-engines as well as in aircraft producing noise (Ceysens *et al.*, 2019). In hydrophones for acoustic damping, 1–3 piezoelectric composites are used. Actuation is also seen with electromagnetic wave absorbing composites for antennas, which are used to send out well defined signals but can be converted to materials that are electromechanically invisible with regard to stealth applications (Smith and Seugling, 2006).

Conclusion

The design of composites for sensors and actuators along with their vital applications are well comprehended to a large extent in spite of their less availability. However, complete experimental confirmation in an application oriented environment will help one to find and close any leftover discrepancies. Specifications, qualification and manufacturing techniques can then be ascertained that may have an impression on further enhancement of existing sensor and actuator materials.

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Multi-Material Production of 4D Shape Memory Polymer Composites

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Introduction

4D printing involves a material that can be transformed after 3D printing upon exposure to an external stimulus. The 4th dimension in 4D printing is time. It is expected that 4D printing of SMPs will have a major influence in the global economy and society in the next decade (Jiang *et al.*, 2017; Tibbitts, 2020). The transformation of a 4D printed object includes expansion/shrinking and flexibility (Leist and Zhou, 2016; Mitchell *et al.*, 2018). 4D printing goes beyond geometrical transformations to include transformations in surface roughness, piezoelectric properties, color, wettability and other functionalities.

SMPs are responsive to various stimuli including water, heat, light and electricity. This unique ability has raised lots of interest within the research community in the last two decades. SMPs have several advantages over shape memory alloys (SMAs) and shape memory ceramics (SMC) such as higher recoverable strain of many hundred percent in comparison to approximate levels of 10% for SMAs and 1% for SMCs. SMPs have low density, low cost and provide ease of fabrication. They can be processed via filled filament fabrication (FFF) and FDM, which are relatively cheaper methods of 3D printing than selective laser melting (SLM) or electron beam melting (EBM) which are commonly used for metal and ceramic 3D/4D printing. 4D printing of polymers usually involves (1) 3D printing of the part followed by (2) shape training, whereby the part is deformed (compressed/stretched) while holding a temperature above the polymer's glass transition temperature (T_g), and finally (3) cooling to a temperature below T_g . The part retains its original shape upon re-heating to a temperature above T_g , hence the shape memory effect (SME). The shape recovery time and temperature of the SMPs can be tailored by a simple adjustment in the matrix composition (Leist and Zhou, 2016; Mitchell *et al.*, 2018).

Consequently, SMPs have the ability to present three stable states including the original shape, the deformed shape and an intermediate shape depending on temperature. Polymers have some disadvantages including a low recovery stress, which is typically in the range of 0.5–3 MPa in comparison to 0.5–1 GPa for metals and ceramics. Another disadvantage of polymers is their low tensile strength and stiffness. Researchers are counteracting these drawbacks by synthesizing SMPs via copolymerization and/or incorporation of nanomaterials in the polymer matrix to enhance mechanical properties. Naturally, polymers do not have conductive or piezoelectric properties. Incorporation of fillers and nanomaterials into the polymer matrix have been investigated for generating electrically actuated SMPs or piezoelectric polymer composites that can be used in flexible sensors and energy harvesters.

In this article, a discussion of 4D printing of SMPs is presented. This article reviews SMPs actuated by heat, electricity, light and water. How 4D printing is being incorporated in various fields including medical, energy, defense, space and electronics is discussed (Mitchell *et al.*, 2018). This article addresses the uses of SMPs in medical devices such as knee implants and in piezoelectric composites such as flexible sensors.

Thermally Activated Shape Memory Polymer Composites

Thermoplastics and thermosets are both used in 4D printing of SMPs (Mitchell *et al.*, 2018). SMPs based on thermoplastics tend to lose their shape recovery ability after a few cycles. Therefore, thermosets are preferable due to their higher stiffness and wider thermal usage range. Shape training for thermally activated SMPs is generally easier than for SMAs. It generally involves heating the polymer to $T > T_g$, followed by stretching/compression (shape fixing) and then cooling to $T < T_g$ while holding the deformation. The original shape is recovered by reheating the part to $T > T_g$.

Tensegrity structures (structures with elements in pure tension and compression) have gained some attention in the literature due to their reduced risk of failure during deployment, which is attributed to their reduced joints and weight. A thermally actuated SMP based on Verowhite and Filaflex was 4D printed to fabricate deployable tensegrities (Fig. 1(A) (i)) (Liu *et al.*, 2017a). The Verowhite-based struts were printed with a commercial 3D printer (Object 260 Connex 3D) and subjected to shape training which involved heating to 65°C, deforming into a flat shape, and finally cooling to 10°C while holding the deformed shape (Fig. 1(A) (ii)). The Filaflex-based elastic cables were printed using the FFF method and attached to the struts. The composite returned to its original shape when heated above the T_g of Verowhite ($T_g = 60^\circ\text{C}$) as shown in Fig. 1(A) (iii).

In Fig. 1(B), polylactic acid (PLA) flat strips were 3D printed and internal strains were induced during shape training (Zhang *et al.*, 2016). The material was capable of changing to a flower shape upon cooling and reversing back to the flat shape upon heating.

Another polymer flower composed of inner and outer petals of different T_g s was 3D printed and shape trained, resulting in a multi-material flower with sequential shape recovery as the temperature was gradually increased. The sequential flower opening

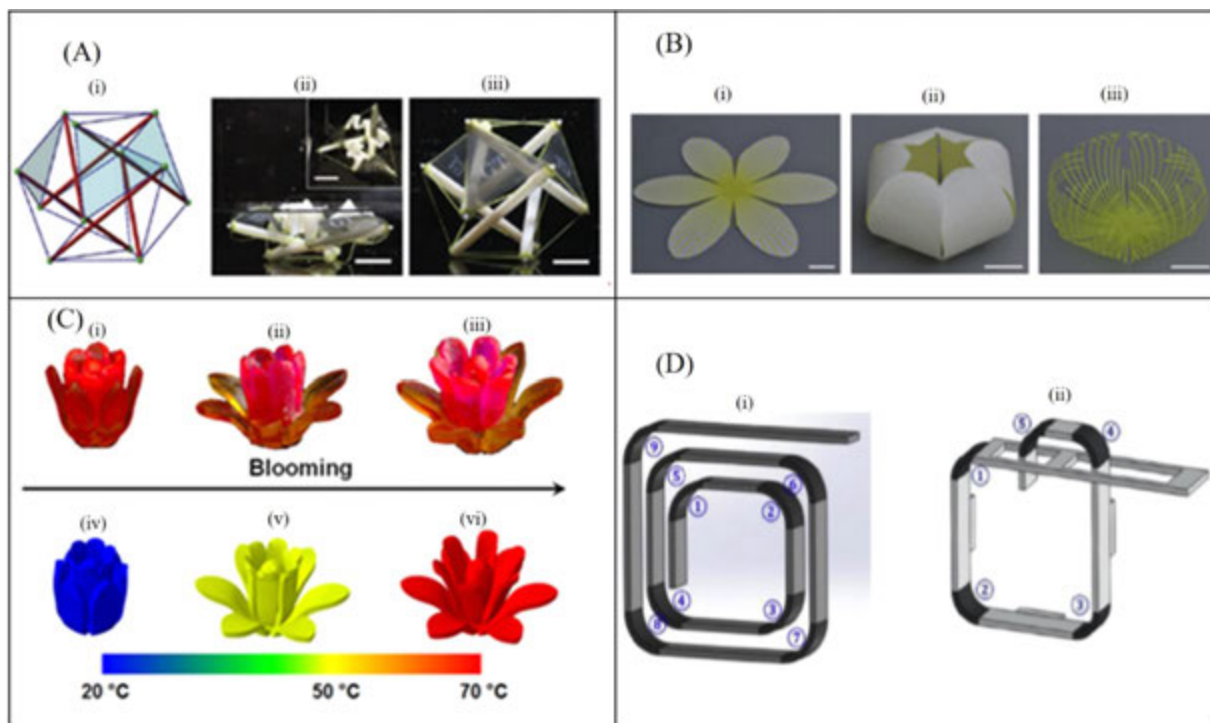


Fig. 1 4D printed thermally activated SMPCs: (A). Tensegrity structures with temperature-controlled deployment. Structures are composed of Verowhite and Filaflex. (B) PLA-based flat 2D strips capable of transforming to a flower upon cooling and reversing to flat shape when heated above T_g of PLA. (C). A multi-material polymer flower with sequential actuation. (D) A multi-material composite with sequential actuation, each hinge has a different T_g giving the sequential actuation property. Reprinted from (A) Liu, K., *et al.*, 2017. Programmable deployment of tensegrity structures by stimulus-responsive polymers. *Scientific Reports* 7 (1), 1–8. doi:10.1038/s41598-017-03412-6 copyright © 2017, with permission from Springer Nature. (B) Zhang, Q., Zhang, K., Hu, G., 2016. Smart three-dimensional lightweight structure triggered from a thin composite sheet via 3D printing technique. *Scientific Reports*, 6, 1–8. doi:10.1038/srep22431 copyright © 2016, with permission of Springer Nature. (C) Ge, Q., *et al.*, 2016. Multimaterial 4D printing with tailorable shape memory polymers. *Scientific Reports* 6, 1–11. doi:10.1038/srep31110 copyright © 2016, with permission of Springer Nature (D) Yu, K., *et al.*, 2015a. Controlled sequential shape changing components by 3D printing of shape memory polymer multimaterials. *Procedia IUTAM* 12, 193–203. doi:10.1016/j.piutam.2014.12.021 copyright © 2015 with permission from Elsevier.

can be seen in Fig. 1(C) (i–iii), while a computer simulation is shown in Fig. 1(C) (iv–vi) (Ge *et al.*, 2016). The outer petals have a higher T_g than the inner petals, resulting in shape shifting occurring in the outer petals first during gradual heating. In Fig. 1(D), sequential actuation is also shown for a part 3D printed with 7 hinges, each with a different T_g (Yu *et al.*, 2015a). Each hinge actuated (changed shape) at a different temperature, resulting in sequential actuation as the device was gradually heated.

Projection microstereolithography was used to fabricate high resolution SMP microgrippers based on photo-curable methacrylate copolymers that form polymer structures due to free radical photopolymerization (Liu *et al.*, 2006; Nguyen *et al.*, 2008; Qi *et al.*, 2008). The microgrippers could be opened and closed depending on the temperature. Thermally activated SMPCs have exciting uses in the renewable energy industry. 4D printed solar energy harvesters based on strips of PLA and paper coated by silver-chrome were proven to have an efficiency increase of about a 25% compared to 3D printed (fixed shape) harvesters, see Fig. 2 (Momeni and Ni, 2018). Each strip of PLA was 80 mm in length, 1 mm in width and 0.2 mm thick as shown in Fig. 2. A CAD model was used to control the LuzBot, Taz 6 printer in printing each PLA strip on a paper sheet. By studying diurnal flowers (parabolic shaped petals) and nocturnal flowers (hyperbolic shaped petals), it was discovered that the parabolic shape is the most efficient at times around 12 pm. The hyperbolic shape was found to be the most efficient at times far from 12 pm. Therefore, a concentrator that has hyperbolic shape at times far from noon and a parabolic shape around noon is ideal. The PLA-paper composite was subjected to a heat treatment to train the shape memory effect. The programming step was done only on one end of the concentrator such that this end would bend towards the silver-chrome layer at high temperatures ($T > T_g$) to produce the parabola shape, and become flat at low temperature ($T < T_g$) to produce the hyperbola shape. This study demonstrated how 4D printing can be used to create an efficient energy harvesting mechanisms using cheap and environmentally friendly materials such as PLA and paper.

Glassy fiber polymers were 3D printed within an elastomeric matrix to fabricate soft parts that could be activated by a combination of heat and stress (Fig. 3(A)) (Ge *et al.*, 2013). CAD modeling was used to control the volume fraction and orientation of the fibers within the elastomeric matrix. Researchers examined various volume fractions of the glassy polymer (0.10, 0.28, 0.40, and 0.60) and various fiber orientations (0° , 15° , 30° , 45° , 60° , 75° , and 90°) along the load direction. Different combinations of volume fraction and fiber orientation led to different shape transformations when the flat strips were heated

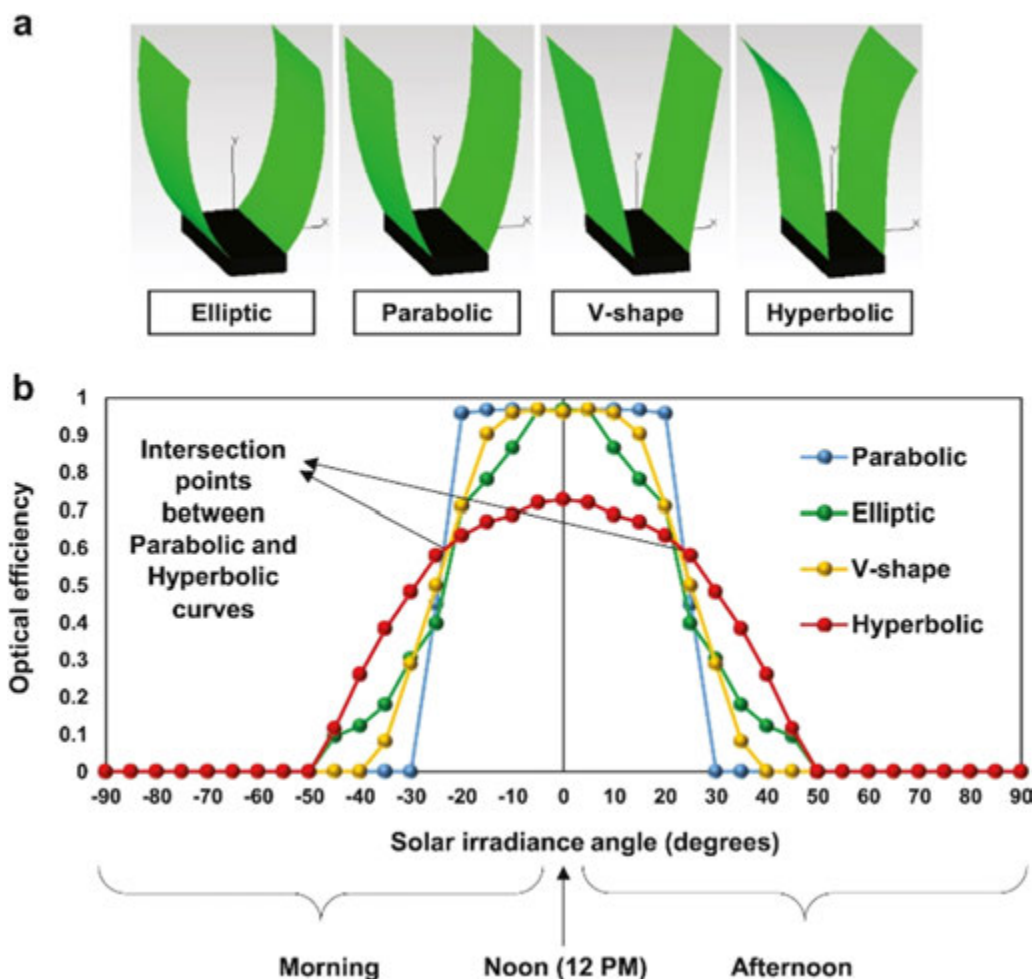


Fig. 2 Solar energy harvesters composed of PLA and paper coated with silver-chrome. The energy harvesters can transform in shape depending on the time of the day thereby increasing energy harvesting efficiency by 25%. Reprinted from Momeni, F., Ni, J., 2018. Nature-inspired smart solar concentrators by 4D printing. *Renewable Energy* 122, 35–44. doi:10.1016/j.renene.2018.01.062 copyright © 2018, with permission from Elsevier.

above T_g as shown in Fig. 3(A) (i–vii). A similar SMPC was used in 4D printing of a self-assembling box (Fig. 3(B)) (Mao *et al.*, 2015). 4D printing also reduces printing time in comparison to 3D printing. For instance, with the same equipment it would have taken about 3 h to 3D print a $20 \times 20 \times 20$ mm hollow box with 1 mm wall thickness, whereas it took about 10 min to print a 2D structure of the box that can transform into a cube after printing (4D printing) (Ge *et al.*, 2014).

Likewise, fillers and nanomaterials have been incorporated into the polymer matrix for mechanical reinforcement (Yan *et al.*, 2013). For example, a 20% increase in shape recovery stress was observed for a polyurethane matrix containing 1 wt% of nanoclays (Cao and Jana, 2007). Carbon nanofillers/carbon nanotubes incorporated in polyurethane for mechanical reinforcement also induced electrical properties (Koerner *et al.*, 2004). PLA-based copolyester nanocomposites with various concentrations of nano-SiO₂ were investigated (Yan *et al.*, 2013) for potential applications in medical devices as they exhibited T_g s below body temperature. Incorporation of Polytetrahydrofuran into PLA allowed the resulting copolyester to have two low glass transition temperatures of -76 and 35°C , which is a significant decrease in T_g from about 60°C (T_g of PLA). The nano-SiO₂ acted as fixed parts when the temperature was above 35°C allowing the composite to remain strong. It was found that pour mixing when incorporating the nanomaterials within the polymer matrix can cause non-uniform dispersion within the SMPC, which causes poor SME.

The ability to tailor the T_g of the polymer is particularly useful in biomedical devices whereby the actuation temperatures need to be close to body temperatures (37°C). SMPCs have been used to print stents capable of changing shape inside the body due to temperature changes, allowing tailored stents to be produced (Zarek *et al.*, 2017). Another potential medical use of 4D printing was demonstrated when PLA based scaffolds with controllable porosity, for the repair of damaged bone, were 3D printed via FFF and subjected to heat treatments to induce the shape memory effect (Senatov *et al.*, 2016). The scaffolds, having a porosity of 30 vol% with an average pore size of $700\ \mu\text{m}$, were capable of retaining their original shape upon heating.

One of the drawbacks of using polymers in implants is their limited mechanical strength. Researchers are implementing ways such as copolymerization and incorporating micro/nanomaterials into the polymer matrix to enhance mechanical properties. PLA scaffolds with 15 wt% hydroxyapatite (HA) particles were 4D printed and compared to those composed of pure PLA in terms of mechanical

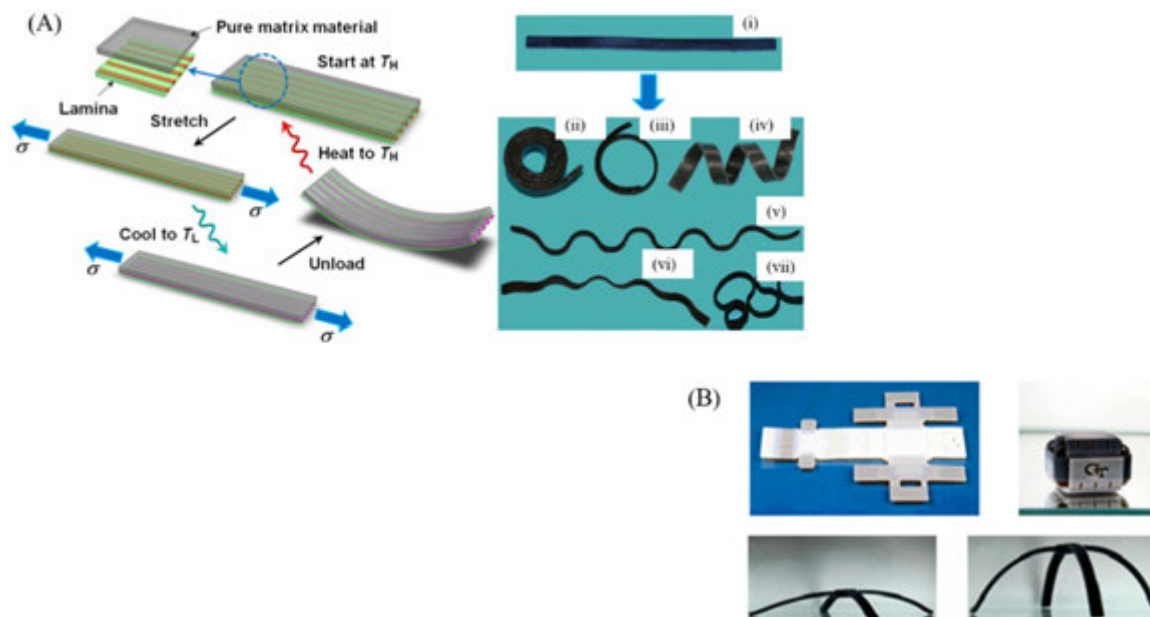


Fig. 3 4D printed thermally activated SMPC. (A). Multi-material composite composed of glassy fiber polymers within an elastomeric matrix. i-vii parts of (A) shows various shapes can be produced upon heating the SMPC depending on the volume fraction and orientation of the fibers within the elastomeric matrix. (B) A self-assembling shape memory box. Reprinted from Ge, Q., Qi, H.J., Dunn, M.L., 2013. Active materials by four-dimension printing. *Applied Physics Letters* 103 (13). doi:10.1063/1.4819837 copyright © 2013, with permission from Applied Physics Letters. (B) Mao, Y., et al., 2015. Sequential self-folding structures by 3D printed digital shape memory polymers. *Scientific Reports* 5, 1–12. doi:10.1038/srep13616 copyright © 2015, with permission from Springer Nature.

properties and degree of shape memory (Senatov et al., 2016). Differential scanning calorimetry (DSC) data reviewed that the added HA particles acts as nucleation sites during the linking of PLA molecular chains and inhibits the motion of molecules. This causes the formation of an additional rigid phase which in turn causes an increase in the recovery stress. A maximum recovery stress of 3 MPa at 70°C was observed for PLA/HA composites, which was 170% higher in comparison to the pure PLA composites. The degree of SME was measured by compressing the scaffolds (deformation) and heating to activate SME. After the first cycle, both the PLA and PLA/HA scaffolds had a 100% recovery in shape, however, the pure PLA scaffolds failed after the second cycle while the PLA/HA scaffolds recovered by 96%. According to the authors, future work would involve bringing the glass-transition temperature of the polymer composite from 60 to 70°C to a temperature close to body temperatures (37°C) so that actuation could be done in-vivo.

Similar work was reported (Senatov et al., 2016) whereby ceramic particles were added to a PLA matrix, causing the reduction in crack growth in the polymer. Another team (Nie et al., 2015) reported that addition of HA particles in PLA matrix increased the toughness and strength of the composite. An increase in shape recovery speed of the PLA matrix due to addition of HA was also reported (Zheng et al., 2006). Similarly, epoxy-based nanocomposites were reinforced with ceramic particles which may contribute to the SME by storing elastic strain (Gall et al., 2004). It was found that by adding particles and also developing copolymers or polymer blends, the SME could be enhanced (Lai and Lan, 2013) (Yan et al., 2013).

Electrically Activated Shape Memory Polymer Composites

FDM was used to 4D print PLA reinforced with carbon fiber to fabricate an electrically activated SMPC with a 95% shape recovery (Zeng et al., 2020) for potential use in lightweight-high strength smart structures. These composites have the capability of shape shifting when subjected to a voltage. The voltage induces heat (resistance heating) which leads to shape change when the temperature reaches the T_g of the polymer. Bending tests were conducted to evaluate printing parameters. It was found that a higher printing speed induced poor mechanical properties, whereas high extrusion temperatures induced higher bending performance and lower surface roughness of the printed components.

A shape memory nanocomposite based on styrene incorporating electromagnetic carbon nanotubes (CNTs) and multiwalled carbon nanotube (MWCNT) nanopaper was developed (Lu et al., 2011) (Fig. 4(A)). The electromagnetic CNTs were vertically aligned using a magnetic field (Fig. 4(B)). The vertical alignment increased conductivity and heat transfer which translated to faster electrical actuation. Various concentrations (0–8 wt%) of CNTs were incorporated into the polymer-carbon nanopaper composite. The study demonstrated that a higher concentration of CNTs results in higher conductivity (lower resistivity). The nanocomposite with 8 wt% CNTs showed the quickest shape recovery (75 s) when subjected to a voltage of 36 V (Fig. 4(A)). The recovery time of 75 s limits the use of the as-fabricated composite to low speed actuations.

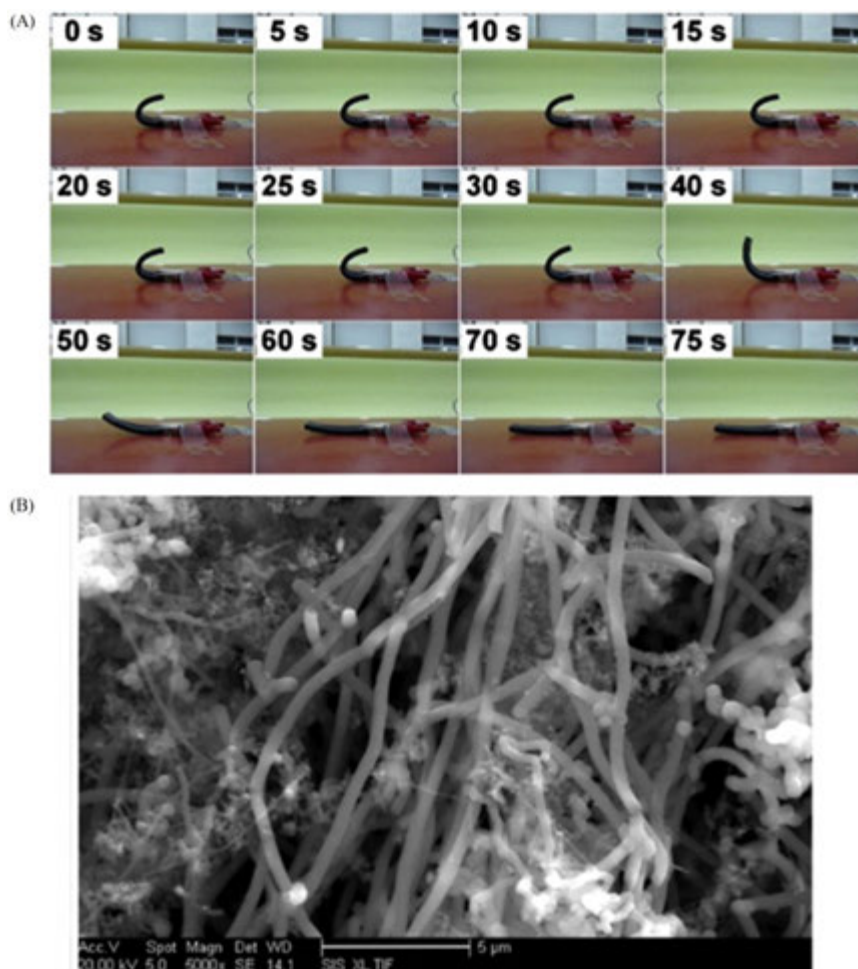


Fig. 4 An electrically actuated SMPC based on Styrene and CNTs. (A). Shape recovery study shows a quickest recovery of 75 s when a 36 V potential difference is applied to a composite with 8 wt% CNT. (B). Scanning electron microscope image of vertically aligned CNTs within the polymer matrix. Vertical alignment of the CNTs increases both thermal and electrical conductivity of the composite. Reprinted from Lu, H., *et al.*, 2011. Magnetically aligned carbon nanotube in nanopaper enabled shape-memory nanocomposite for high speed electrical actuation. *Applied Physics Letters* 98 (17), 1–4. doi:10.1063/1.3585669 copyright © 2011, with permission from Applied Physics Letters.

Conversely, a fast-response shape memory polymer composite with a shape recovery time of 2 s was reported (Luo and Mather, 2010). The shape memory polymer was composed of diglycidyl ether of bisphenol-A (DGEBA), neopentyl glycol diglycidyl ether (NGDE), and poly(propylene glycol) bis(2-aminopropyl) ether (Jeffamine D230) of various compositions. This polymer composite had a T_g that could be easily programmed by copolymerization of DGEBA and NGDE at various ratios. The polymer had good cycle lifetime with chemical and thermal stability. Conductive carbon nanofillers (CNFs) were added to the polymer composite to induce electrical responsiveness. This allowed DC voltages of 10, 15 and 20 V to be used as actuation mechanism for the shape memory polymer. It was found that a higher actuation voltage gave a faster electrical response. The addition of CNFs did not affect the glass transition temperatures according to DSC analysis. However, the CNFs increased the rubbery modulus from 10 to 200 MPa. This increase led to higher stresses in shape memory recovery. Electrical conductivity was measured using a four-point-probe and values up to 30.59 Sm^{-1} were obtained. The recovery ratio, R , is given by

$$R(\%) = \frac{\theta_i + \theta(t)}{\theta_i - \theta_e} \times 100\%$$

where θ_i , $\theta(t)$, θ_e are the initial deformation angle of the fixed sample, the deformation angle at a given time t and the deformation angle at the equilibrium state, respectively. This equation was also used to measure recovery rate in other reports (Lu *et al.*, 2011). The measurements involved taking several images as the shape recovers while accurately timing each image.

CNTs were also incorporated into a polymer resin to increase the T_g and the viscosity as well as to enhance the mechanical and electrical properties (Rodriguez *et al.*, 2016). The conductivity of the composite was increased from 0.001 to 0.4 S cm^{-1} by an increase in CNTs concentration from 0.6 to 5.6 vol%. The conductive composite was shape trained and could recover its original shape upon heating above 85°C in an oven. The structure was connected to a voltage supply (9 V) and completed a circuit

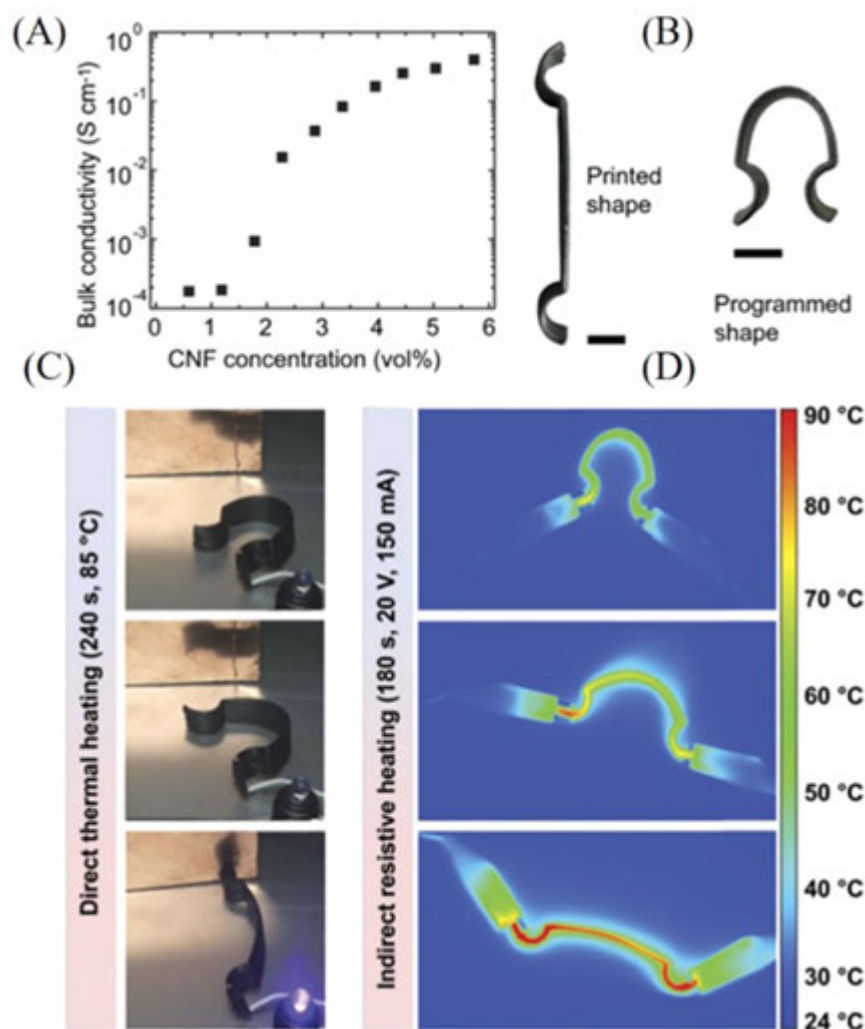


Fig. 5 4D printed electrically-activated interconnects. The SMPC changes shape upon subjection to a voltage. The shape change allows the part to complete a LED circuit, demonstrating the potential use of the composite in electrical interconnects. A higher concentration of CNFs within the polymer matrix leads to a higher electrical conductivity. Reprinted from Rodríguez, J.N., *et al.*, 2016. Shape-morphing composites with designed micro-architectures. *Scientific Reports* 6 (June), 1–10. doi:10.1038/srep27933 copyright © 2016, with permission from Springer Nature.

connection upon recovering its original shape which switched on an LED (Fig. 5). The composite was promising for use in electrical interconnects and thermal sensors.

An epoxy-based SMP obtained from co-reacting L552 epoxy resin and K552 amine hardener and blending unidirectional carbon fibers was used to fabricate rectangular strips with SME (Murugan *et al.*, 2017). The strips could revert to their original shape when a current was passed through them due to resistance heating. The carbon fibers were cut into 300 × 100 mm and incorporated into the polymer matrix to generate strips with a fiber-to-matrix ratio of 30:70. Three different strips, each with different number of layers (1, 2 and 3) were fabricated and tested. The addition of more carbon layers increased the shape fixity (stiffness) of the strip resulting in slower shape recovery. It was concluded that shape recovery and fixity were chiefly dependent on the number of carbon layers and the applied electrical power. The 2-layered strip recover 100% of its original shape, whereas the 1-layered and the 3-layered strips recovered 96% and 90% of their original flat shape respectively.

Magnetic nanoparticles of Fe₃O₄ were also incorporated in a PLA-based SMPC matrix (Wei *et al.*, 2017) that could be remotely actuated via heating by an alternating magnetic field. The 4D printed PLA composite was used to fabricate a shape shifting intravascular stent which could be externally guided by a magnet. A material that responded to electromagnetic waves was also developed for sensing blood pressure insulin levels (Ivanova *et al.*, 2013).

Piezoelectric Application

Piezoelectric materials are able to generate electricity when subjected to stress and vice versa. Piezoelectric materials include polycrystalline ceramics such as barium titanate, lead lanthanum zirconium titanate and zirconium titanate (Polla and Francis, 1998).

Piezoelectric materials also include polymers such as polyvinylidene fluoride (PVDF), single crystal materials such as quartz and zinc oxide, and organic crystals such as ammonium dihydrogen phosphate. These materials are extensively used in manufacturing pressure sensors, vibration sensors and energy harvesters. Traditionally, the aforementioned are produced via solution deposition and chemical/physical vapor deposition onto a planar surface (Polla and Francis, 1998; Li *et al.*, 2006, 2007). These planar deposition manufacturing methods are limited to 2D geometries. Additive manufacturing has allowed the manufacturing of 3D/4D piezoelectric components (Sun and Zhang, 2002; Kim *et al.*, 2014; Woodward *et al.*, 2015; Chen *et al.*, 2016). Stereolithography was reported in the printing of piezoceramics such as barium titanate (Kim *et al.*, 2014; Chen *et al.*, 2016), lead magnesium niobate titanate (Woodward *et al.*, 2015) and zirconate titanate (Sun and Zhang, 2002). The brittleness of piezoelectrics limits their printability/uses which makes piezoelectric polymers favorable due to their higher ductility. PVDF piezoelectric polymer has been widely printed via several methods including FDM (Lee and Tarbuton, 2014) and ultrasonic additive manufacturing methods (Hahnlen and Dapino, 2010). PVDF has a high piezoelectric coefficient and is flexible, making it very useful in biomedical devices (Abdelhamid *et al.*, 2012; Martins *et al.*, 2014; Ramadan *et al.*, 2014). PVDF is not photocurable and the addition of a solvent is required for stereolithography printing.

PVDF combined with diethyl fumarate as a solvent was printed via projection micro stereolithography (PμSL) to produce a V-ink (a piezoelectric photocurable resin) (Chen *et al.*, 2017). The viscosity of the V-ink was controlled by varying the concentration of the solvent. The printed objects were thin rectangular films of 9.9 mm length, 7.4 mm width and a thickness that was varied from 0.1 to 0.9 mm. To measure the piezoelectric coefficient (g_{33}) of the printed parts, two thin aluminum plates were placed to sandwich the PVDF object and a force was applied onto the plates. Electrodes were attached to the aluminum plates to measure the induced voltage due to the applied force. The output was recorded via an oscilloscope. It was found that a higher concentration of PVDF particles within the V-ink increased the piezoelectric coefficient. However, a concentration limit of 35 wt% of PVDF was required for acceptable viscosities (printability). The piezoelectric coefficient of the material increased by 60.1% (from 14.62 to 23.42 mV m/N) when the concentration of PVDF was increased from 15 to 35 wt%. A decrease in the poling electric field from 1.33 to 12.00 MV/m was witnessed when the thickness of the piezoelectric PVDF film decreased from 0.9 to 0.1 mm.

Naturally, most polymers do not have piezoelectric properties but, thanks to the possibilities of additive manufacturing, the addition of particles exhibiting such properties into the polymer matrix gives the resulting composite piezoelectric properties. The generated composite combines the flexibility properties of the polymer and the piezoelectric properties of the added particles. A piezoelectric material made from ferroelectric microparticles incorporated into a polymer matrix was used to 4D print a biomedical sensor for knee implants (Grinberg *et al.*, 2019). This piezoelectric material produces self-powering knee implants with sensing capability such as temperature, life span estimates and communication such as WI-FI/Bluetooth (Fig. 6(A)). This allows

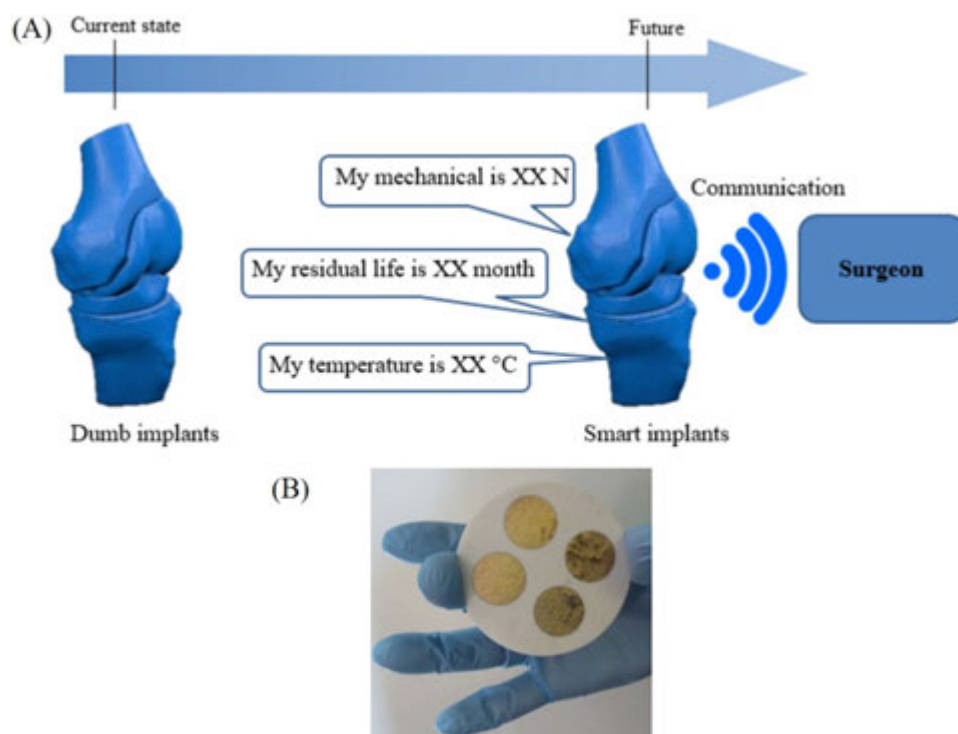


Fig. 6 Futuristic 4D printed knee implant with sensing capabilities such as temperature and communication ability such as Wi-Fi. (A). A comparison of current 3D printed knee implants and futuristic 4D printed implants with advanced capabilities such as damage detection. (B). Polymer- BaTiO₃ based piezoelectric sensors that can be placed within the implant for sensing purposes. Reprinted from Grinberg, D., *et al.*, 2019. 4D Printing based piezoelectric composite for medical applications. *Journal of Polymer Science, Part B: Polymer Physics* 57 (2), 109–115. doi:10.1002/polb.24763 copyright © 2019, with permission from John Wiley and Sons.

surgery to be more efficient and provides comfort to the patient. FFF technique was used to print the piezoelectric material using a commercial printer, an Ultimaker 3D printer. Polyamide (PA11) and ferromagnetic particles of barium titanate (BaTiO_3) were combined via solution casting and filaments were produced to feed the 3D printer. Circle-shaped sensors of a diameter of 20 mm and a thickness of 2 mm were printed as shown in Fig. 6(B). Compression force was applied to the printed structures and measured precisely by a load cell. The piezoelectric coefficient was determined via a Kistler Amplifier Charge Meter Type 5015A. It was discovered that there was a linear relationship between the volume fraction of the BaTiO_3 particles of size 700 nm and the piezoelectric properties. It was also observed that the piezoelectric coefficient dramatically improved when the BaTiO_3 particle size was increased from 100 to 300 nm. The larger particles favored uniform distribution into the polymer matrix which leads to better piezoelectric properties.

Recently, the interest on flexible piezoelectric pressure sensors has significantly grown as highlighted by Luo and co-workers in a review paper (Lou *et al.*, 2019). For example, a contact printing method was used to print Ge/Si core/shell nanowires (NW's) on polyimide to generate a pressure sensor (Takei *et al.*, 2010). Inkjet printing has been widely used for manufacturing of pressure sensors due to its ease of use and affordability. Piezoresistive mechanical sensors made from carbon and trichlorosilane modified paper has been produced via inkjet printing (Lessing *et al.*, 2014). In another report, Ag NW's and double-hydroxide inks were printed on paper substrates to generate a flexible human motion sensor with nontoxicity and competitive sensing ability (Wei *et al.*, 2015).

4D printed piezoelectric nanomaterials have shown lots of potential in nanomedicine for the actuation of the nervous tissue and stimulation of cells such as skeletal myotubes and osteoblasts (Askari *et al.*, 2018). A variety of materials have been used in the 4D printing of nanotransducers including boron nitride, zinc oxide and barium titanate. The choice of material is on the basis of level of biocompatibility, commercial availability and piezoelectric effects. Boron nanoparticles has been proven to be biocompatible both in vitro (Ciofani *et al.*, 2014) and in vivo (Ciofani *et al.*, 2013; Xin *et al.*, 2020) studies, this allows them to be used in large amounts. B nanoparticles are commercially available (Ciofani and Mattoli, 2016) and they have good piezoelectric properties due to their perovskite structure (Deng *et al.*, 2010).

A piezoelectric polymer based on polyvinylidene fluoride trifluoroethylene (P(VDF-TrFE)) and silver nanoparticle-based electrodes were inkjet printed to develop actuators (Pabst *et al.*, 2013). A sandwich-like structure was developed whereby the piezoelectric polymer was placed between two silver electrodes. The structure bended upon the application of a voltage, presenting the 4D effect. The piezoelectric coefficients (d_{31}) were found to be approximately $7\text{--}9 \text{ pm V}^{-1}$, which allowed sufficient deflection for actuation. These actuators have a promising use as micropumps. Currently, micropump actuator elements are produced separately and then assembled. However, with inkjet printing the whole actuator can be fabricated at once, reducing production costs and time.

With the increasing global energy demand and an increase in the fabrication of portable electronic devices, energy harvesting technologies have gained an interest in research. Flexible piezoelectric generators based on poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) and SWCNT ($<0.05 \text{ wt}\%$) were fabricated via extrusion printing (Shepelin *et al.*, 2020). The incorporation of the SWCNT into the polymer matrix was proven to enhance the piezoelectric charge coefficient (d_{33}) by up to 500%. A power density of up to $71 \text{ }\mu\text{W cm}^{-3}$ was reported. The composite could be recycled easily using a green solvent (acetone).

Light Stimulated Shape Memory Polymer Composites

Light actuation has an advantage over other actuation methods (water, heat, etc.) because stimuli can be induced remotely. Magnetic field actuation can also be induced remotely however, the distance from the magnetic field is limited. Light is an effective activation technique because it is controllable and an abundant source of energy. Light actuated SMPCs have been used in applications related to self-assembly structures, complex folding methods, transformative surface deformations (Ubukata *et al.*, 2007; Kravchenko *et al.*, 2011), UV sensor and filters (Kim *et al.*, 2010), and soft robotics. Some 4D printing research that uses light-activated materials actually uses the heat from the light source to activate the shape change properties. Light actuation methods have several advantages over others including remote actuation, abundance of sources of light and ease of controllability. However, it can be difficult to transform light to mechanical/heat energy for use in SMPCs so nanomaterials are often incorporated into the polymer matrix to ease that transformation. Other methods of actuation require human interaction to pre-strain the material, actuate and the release of strain for transformation. Light actuated devices could prevent this need and fully automate the process (Leist and Zhou, 2016).

The photothermal effect involves the generation of thermal energy from electromagnetic radiation (light). Some shape memory polymers can absorb light at various wavelengths which allows them to change shape after the temperature goes beyond the T_g (Jeong *et al.*, 2020). Nanoparticles and photothermal fillers can be incorporated into the polymer matrix to develop light actuated SMPC (Zhang and Zhao, 2013; Shou *et al.*, 2014; Webb and Bardhan, 2014; Fang *et al.*, 2017; Herath *et al.*, 2018). Examples of photothermal fillers include gold nanoparticles/nanorods/nanospheres (Zhang *et al.*, 2012; Zhang and Zhao, 2013; Zhang *et al.*, 2013). Different polymers have been used as matrix material for gold nanostructures in the development of light actuated SMPCs including polyurethane (Xiao *et al.*, 2013; Li *et al.*, 2018), polyvinyl acetate (PVA) (Zhang *et al.*, 2013) and bisphenol A diglycidyl ether (Leonardi *et al.*, 2015; Zheng *et al.*, 2015). Silver nanoparticles are more affordable than gold nanoparticles and are known to have a ten-fold photothermal effect (Toncheva *et al.*, 2018; Yenpech *et al.*, 2019). Silver also exhibits antibacterial effects and is currently used in wound healing devices making it a good candidate for biomedical applications (Paladini and Pollini, 2019).

Nanostructured titanium nitride (Ishii *et al.*, 2016), tungsten oxide (Zhou *et al.*, 2019) and carbon (Liu *et al.*, 2017b) have been also incorporated into SMPCs to create light actuated SMPCs. Carbon nanomaterials have an advantage over gold/silver for use in 4D printing because they are relatively cheap and biocompatible. Carbon nanoparticles have been produced via a 'green' method

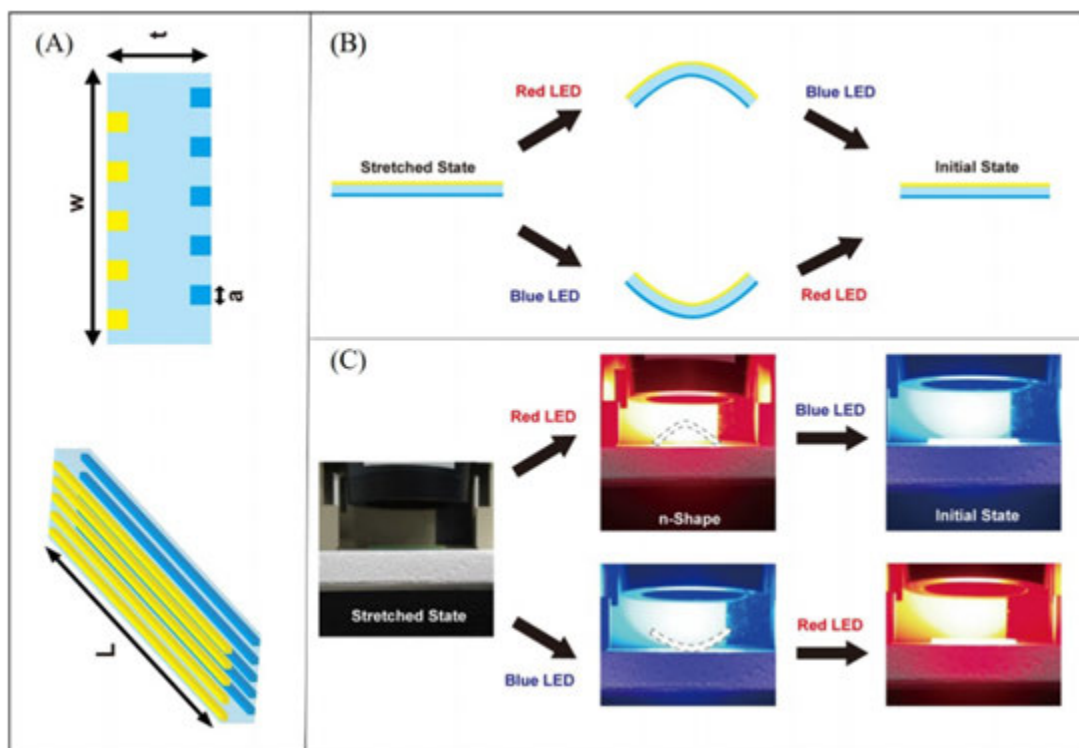


Fig. 7 A light-responsive composite with 3 different shapes depending on the light source. (A). As printed part without submission to neither red nor blue light. (B–C). The polymer transforms to either of two shapes depending on the type of light it is subjected to. An “n” shape is observed when red light is present first and an “u” shape is observed when blue light is present first. The material transforms to its original shape when both blue and red light are applied in sequence. Reprinted from Jeong, H.Y., *et al.*, 2020. Multicolor 4D printing of shape-memory polymers for light-induced selective heating and remote actuation. *Scientific Reports* 10 (1), 1–11. doi:10.1038/s41598-020-63020-9 copyright © 2020, with permission from Springer Nature.

called pulsed laser ablation in liquid (PLAL) which involves the use of a laser to irradiate the target (carbon) to generate carbon nanoparticle colloids (Al-Hamaoy *et al.*, 2014; Bagga *et al.*, 2015, 2017). PLAL has been used to develop nanoparticles of other materials including silicon (Yang *et al.*, 2009), iron (Muniz-Miranda *et al.*, 2017) and titanium (Semaltianos *et al.*, 2010), making it a promising method of synthesizing nanoparticles for use in 4D printing. Carbon nanomaterials have been incorporated in epoxy based resin (Lu *et al.*, 2014; Yu *et al.*, 2015b), polydimethylsiloxane (Ahir and Terentjev, 2005) and polyurethane (Yi *et al.*, 2014) to develop light activated SMPs.

Two commercial shape memory polymers of different colors namely Veroyellow (yellow colored) and Verocyan (blue colored) were printed as rectangular fibers as shown in Fig. 7(A) and B ($L = 40$ mm, $w = 5.5$ mm, $t = 2$ mm, $a = 0.4$ mm) (Jeong *et al.*, 2020). The blue polymer can absorb red light while the yellow polymer absorbs red light. The absorption of light raises the temperature. The shape of the polymer changes when $T > T_g$. Both polymers have a T_g of 66.7°C . The printed composite was shape-trained by stretching it horizontally (10% strain) in water at 90°C and then holding this shape while cooling the composite to 25°C . The composite changed to an “n” shape when subjected to a red LED for 30 s. On the other hand, the composite changed to an “u” shape when subjected to a blue LED for 30 s. This is because, when the polymer is subjected to red light (red LED), only the blue fibers absorb this light and these transform back to the original shape leaving the yellow fibers in their stretched shape. When blue light is applied first the reverse is also true; the yellow fibers return to their original shape while the blue fibers remain stretched leading to the “u” shape (top of Fig. 7(B) and (C)). When blue light is applied followed by red light, the whole composite changes to its original shape. A similar phenomenon is observed when red light is applied first followed by blue light, this is shown in (bottom of Fig. 7(B) and (C)). In other work, a SMP that could fold upon exposure to light was 4D printed via inkjet printing (Liu *et al.*, 2012; Lee *et al.*, 2015). Similarly, different colors of light were used to induce sequential folding in a SMP composite (Lee *et al.*, 2015; Liu *et al.*, 2017c).

Multiphoton lithography (MPL), also known as direct laser writing, provides high resolution (around 200 nm) and has been used to print both rigid materials (e.g., acrylic and epoxy resin) and soft materials (e.g., hydrogels). Light-responsive disk-shaped microcomposites ($\varnothing = 30$ μm , $h = 5$ μm) were 4D printed via the MPL (Nishiguchi *et al.*, 2020). The composites were made from light-responsive gold nanorods (AuNRs) and a thermoresponsive polymer called poly(N-isopropylacrylamide) (PNIPAm). The polymer swelled when its temperature raised above a certain transition temperature (T_g) and returned to its original shape when the temperature was below T_g . Field-emission scanning electron microscopy confirmed the successful incorporation of the nanorods into the polymer. These AuNRs have plasmonic effects; they can be heated when exposed to light of wavelengths 620 and 810 nm. These wavelengths are called the longitudinal plasmon absorption. The wavelength could be altered by changing the

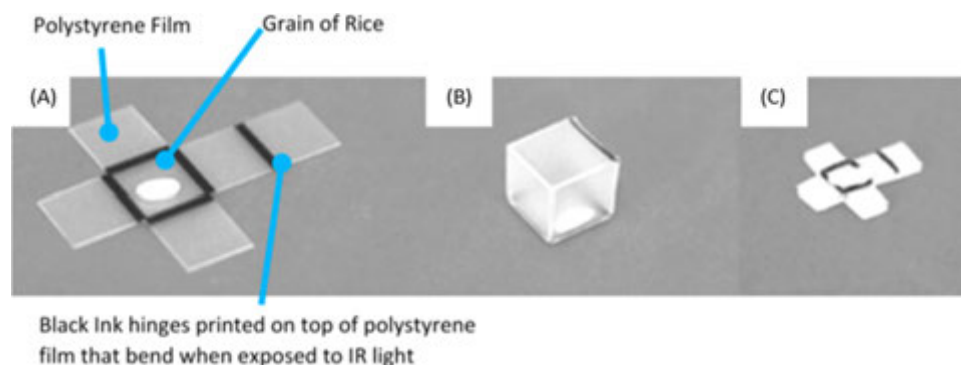


Fig. 8 A 4D printed self-assembly box capable of encapsulating a small object such as a grain of rice. (A). The as printed 2D shape. (B). Shape transformation when the light actuated SMPC is subjected to IR light. (C). The original shape restored when the light source is removed. Reprinted from Liu, Y., *et al.*, 2012. Self-folding of polymer sheets using local light absorption. *Soft Matter* 8 (6), 1764–1769. doi:10.1039/c1sm06564e copyright © 2012, with permission from Springer Nature.

aspect ratios of the AuNRs. The heated nanorods transferred the thermal energy to the thermoresponsive SMP causing the polymer to swell. The density of the printed structure was varied by changing the hatching/slicing distance during printing (300 – 500nm). It was found that varying the density of the printed object changes the swelling/deswelling behavior of the polymer. A decrease in the printing density provided a more dynamic gel with higher amplitudes in thermal responsiveness. These light-responsive smart materials could find applications in micro-optomechanical systems, microfluidic systems and as microswimmers robots.

In robotics, 4D printed actuators remove the need for on-board power, processors and motors (Camacho-Lopez *et al.*, 2004; Milam *et al.*, 2010). This reduces the weight, size and cost of the robots significantly. An interesting light-driven microbot based of liquid crystal film (LCLCF) composed of azobenzene chromophores was 4D printed (Huang *et al.*, 2015). The microbot bended when exposed to UV light and reverted to the original shape upon exposure to white light.

Another interesting application of light actuated SMPCs is presented in Fig. 8, where a self-assembling cube capable of encapsulating a small object such as a grain of rice was 4D printed (Liu *et al.*, 2012). Inkjet printing was used to print the hinges (composed of black ink) onto flat, pre-stressed polystyrene films. Infrared light was used to heat the composite to a temperature above the T_g of the composite. Areas in vicinity to the black ink reached T_g faster. This caused bending at these regions producing a cube shape (Fig. 8(B)). The shape reverted to flat when the entire composite was heated to above T_g (Fig. 8(C)).

Water Actuated Shape Memory Polymer Composites

As one of the most accessible and abundant materials available, water is a great utility in the field of 4D printing for effective activation of shape memory effects in SMPCs. Water stimulated 4D printed devices are mostly based on hydrophilic and moisture absorbent materials that can swell when exposed to water and on thermally activated hydrogels that can react to water temperature changes (i.e., hot water or cold water to heat or cool the material, respectively) (Lee *et al.*, 2017; Ali *et al.*, 2019; Nam and Pei, 2019; Zhang *et al.*, 2019). Water is also ubiquitous within the human body and, consequently, 4D printed biocompatible devices show great promise for in-vivo and biomedical applications (Miao *et al.*, 2017; Shie *et al.*, 2019). The composite character of these devices also allows for stronger, more durable devices with diverse morphologies (Lee *et al.*, 2017; Ali *et al.*, 2019).

The adaptable morphology of a hydrogel is well documented in their ability to absorb large amounts of water or biological fluids (Dong *et al.*, 2020). Through dehydration and rehydration, once 3D printed these naturally become 4D materials. Highly complex designs were recently created through the use of SMPCs that were altered through water immersion (Sydney Gladman *et al.*, 2016). In this work, plant-inspired biomimetic hydrogel structures embedding stiff cellulose fibrils were 3D printed and cured to produce an acrylamide matrix that exhibited anisotropic swelling upon immersion in water. This was accomplished by the express uptake of water in the interfibrillar spaces through the filament radius ($\sim 100 \mu\text{m}$) which led to the shape alteration in a matter of minutes. The behavior of this device allowed for the response to be observed in the longitudinal and transverse direction. The biocompatibility and flexible ink design allowed for complex designs that could be dynamically reconfigured with tuneable functionality. This novel process allowed the synthesis of a biomimetic material that can be implemented in tissue engineering, biomedical devices or soft robotics.

The manipulation of a SMPC device can be simply done by utilizing different T_g of the material to demonstrate self-folding and opening properties, as shown by Wu *et al.* who use 2 different polymer fibers, one with a higher T_g ($\sim 57^\circ\text{C}$) and one with a lower T_g ($\sim 2^\circ\text{C}$) (Wu *et al.*, 2016). This difference in T_g s allows for shape manipulation in water by raising or lowering the temperature. Design will determine function in such that this may be used to grab/pick up items below water (see Fig. 9) or create rigid complex designs that display self-folding and opening abilities through temperature manipulation.

A combination of water immersion for material swelling, followed by temporal manipulation of its temperature-dependent modulus to regulate the time of the shape change, determines the high strength these composite materials can achieve. This approach was successfully demonstrated for a “ladder” shaped design based on three different materials, i.e., a hydrogel, an SMP and an

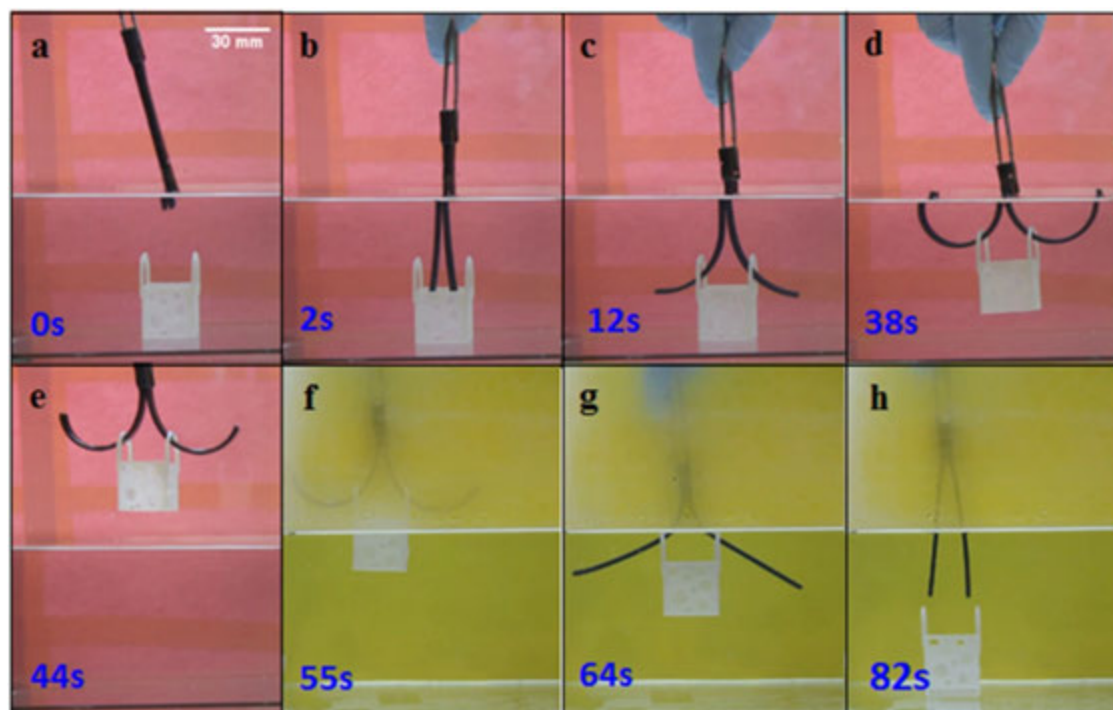


Fig. 9 A water actuated SMPC capable of picking up objects underwater by gradually transforming shape as it is lowered under water. Reprinted from Wu, J., *et al.*, 2016. Multi-shape active composites by 3D printing of digital shape memory polymers', Scientific Reports 6, 1–11. doi:10.1038/srep24224 copyright © 2016, with permission from Springer Nature.

elastomer. The “ladder” became convex when swollen through water immersion, and was then solidified by heating to 75°C followed by cooling to fix its rigidity (Mao *et al.*, 2016). This concave shape could hold a 50 g load without any deformation. It could also regain its flat “ladder” shape through heating to 75°C once again, exhibiting a reversible behavior. A two-way reversible actuator based on the same premise and hydrogel-shape memory polymer-elastomer layer combination was also developed allowing for a strong, shape changing material that could be used in areas such as engineering or biomedical applications (Mao *et al.*, 2016). These characteristics would not be possible if the proposal was not de using multi-material design. Similarly, a smart valve that responded to the surrounding temperature was also based on a composite hydrogel (Bakarich *et al.*, 2016). The valve would open or close depending on the water temperature. At 20°C the valve was open but closed at 60°C. The valve was printed using alginate (Alg)/poly (acrylamide) (PAAm) ionic covalent entanglement (ICE) gel. In terms of strength, it was demonstrated that this material had better mechanical properties when printed instead of cast, as would be normally done for hydrogel synthesis.

Pharmaceutical Application

Recent advances in 4D printing technology and smart materials are leading to the production of a user friendly cost effective and highly efficient drug delivery mechanism. 4D printed minimally invasive drug delivery pods use morphology transformations to unfold. One can envisage a similar use of 4D printing in conformal wounds, the sealing of bone defects, and the enhancement of tissue regeneration. The application of 4D printed pharmaceutical drugs presents a novel polymer composite for clinical situations though much more research is required in this area. In 4D printing technology, the smart material-based devices or structures are manufactured using 3D printers and these smart materials have already been shown in drug delivery pharmaceutical applications. Advanced polymer materials having controlled drug release (delayed release or quick release) functionalities according to its biodegradability have been developed (Lendlein and Langer, 2002). Shape-memory polymer based pharmaceutical products can also release drugs in a controllable manner, see Fig. 10. Using smart materials, it is possible to tailor/customize drug delivery devices according to a user's needs. This makes smart materials attractive for biomedical applications and industries. Such devices for drug loading can be designed with a targeted release location, lower and bespoke amount of drug dose when compared to traditional oral administration.

The biodegradable shape memory polymer based on chemically cross-linked polymeric networks of branched oligo-(εcaprolactone) exhibit approximately 100% strain recovery rate (Nagahama *et al.*, 2009). This material exhibits enhanced temperature sensitive shape recovery. Thermo-responsive multi-fingered grippers based on the poly(propylene fumarate) sections and stimuli-responsive poly(N-isopropylacrylamide-co-acrylic acid) were developed for drug release in a controllable manner for targeting the gastrointestinal tract (Malachowski *et al.*, 2014). Once this device exposed to body temperature after insertion in to the human body, it starts to grip onto gastrointestinal tracts and release the drug. Such devices could be capable for targeted drug

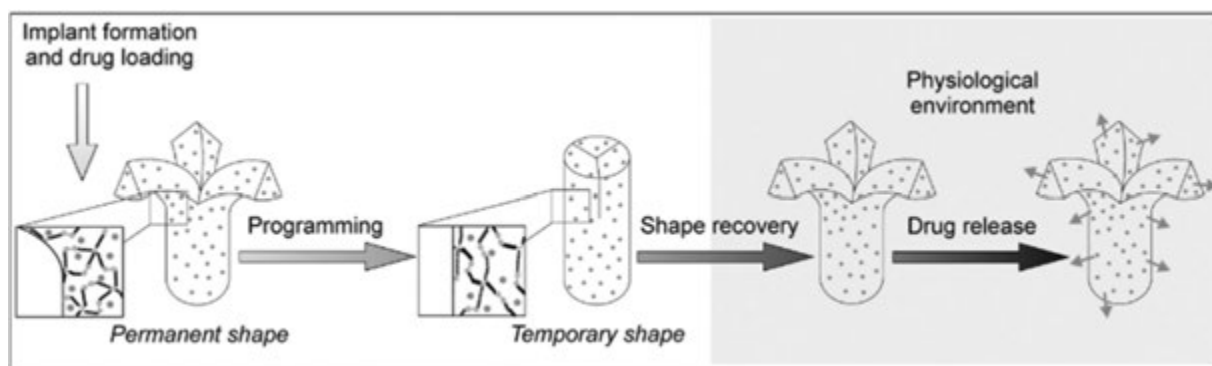


Fig. 10 Shape memory polymer based shape recovery and drug release. Reprinted from Wischke, C., *et al.*, 2009. Evaluation of a degradable shape-memory polymer network as matrix for controlled drug release. *Journal of Controlled Release* 138 (3), 243–250. doi:10.1016/j.jconrel.2009.05.027. copyright © 2009, with permission from Elsevier.

delivery and these devices based on smart materials can be developed cost effectively using 4D printing. The stimulus could be the pH level, electromagnetic energy wavelength, or biological fluid concentration. 4D printed devices could therefore be used to load pharmaceutical drugs and release them in a controlled manner into the particular environment when that environment offers the drug releasing device with the required suitable stimulus (Zhang *et al.*, 2019).

Conclusion

SMPCs can be categorised by their actuation method. We have reviewed SMPC actuated by thermal energy, electricity, light and water. It is worth noting that other actuation methods exist including pH (Han *et al.*, 2012) however, the types reviewed in this article are predominant in literature. We reviewed many SMPCs in this article. We have seen that the T_g of the polymer is crucial, it is the trigger point at which shape transition occurs. The T_g can be tailored easily by copolymerization at different concentrations and/or addition of nanomaterials into the polymer matrix. Polymers have poor mechanical properties. Incorporation of nanomaterials into the polymer matrix can also enhance the poor mechanical properties of polymers. The nanomaterials act as nucleation sites within the polymer which reduces the mobility of molecules thereby increasing mechanical strength. Light actuated SMPCs have been deemed to be very promising relative to other actuations methods due to the ability for remote actuation. Light actuated SMPCs also allow sequential/selective actuation by the use of different materials that absorb light of different wavelengths. This article also reviewed the implementation of shape memory polymer composites within piezoelectric and drug delivery applications. Piezoelectrics play a major role in energy harvesting and the fabrication of flexible sensors. Throughout this article we have seen examples of SMPCs being used in various fields including medical, electronics, automation, and energy, which highlights the importance of this growing research field for the future.

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